



This is a digital copy of a book that was preserved for generations on library shelves before it was carefully scanned by Google as part of a project to make the world's books discoverable online.

It has survived long enough for the copyright to expire and the book to enter the public domain. A public domain book is one that was never subject to copyright or whose legal copyright term has expired. Whether a book is in the public domain may vary country to country. Public domain books are our gateways to the past, representing a wealth of history, culture and knowledge that's often difficult to discover.

Marks, notations and other marginalia present in the original volume will appear in this file - a reminder of this book's long journey from the publisher to a library and finally to you.

### Usage guidelines

Google is proud to partner with libraries to digitize public domain materials and make them widely accessible. Public domain books belong to the public and we are merely their custodians. Nevertheless, this work is expensive, so in order to keep providing this resource, we have taken steps to prevent abuse by commercial parties, including placing technical restrictions on automated querying.

We also ask that you:

- + *Make non-commercial use of the files* We designed Google Book Search for use by individuals, and we request that you use these files for personal, non-commercial purposes.
- + *Refrain from automated querying* Do not send automated queries of any sort to Google's system: If you are conducting research on machine translation, optical character recognition or other areas where access to a large amount of text is helpful, please contact us. We encourage the use of public domain materials for these purposes and may be able to help.
- + *Maintain attribution* The Google "watermark" you see on each file is essential for informing people about this project and helping them find additional materials through Google Book Search. Please do not remove it.
- + *Keep it legal* Whatever your use, remember that you are responsible for ensuring that what you are doing is legal. Do not assume that just because we believe a book is in the public domain for users in the United States, that the work is also in the public domain for users in other countries. Whether a book is still in copyright varies from country to country, and we can't offer guidance on whether any specific use of any specific book is allowed. Please do not assume that a book's appearance in Google Book Search means it can be used in any manner anywhere in the world. Copyright infringement liability can be quite severe.

### About Google Book Search

Google's mission is to organize the world's information and to make it universally accessible and useful. Google Book Search helps readers discover the world's books while helping authors and publishers reach new audiences. You can search through the full text of this book on the web at <http://books.google.com/>

A-5 A 127

HARVARD UNIVERSITY



LIBRARY OF THE  
BIOLOGICAL LABORATORIES  
*From*  
HARVARD COLLEGE LIBRARY

MAY 4 1949



三

三

一

一

一

一

一

一



THE JOURNAL  
—OF THE—  
AMERICAN CHEMICAL SOCIETY.

---

VOLUME XXIV.

1902.

---

COMMITTEE ON PAPERS AND PUBLICATIONS

WILLIAM A. NORTON, Editor

W. F. HENDERMAN

WM. MCWILLIAMS

EDGAR F. SMITH

H. P. TAYLOR

EDWARD EAST

J. H. LONG

ALBERT A. SQUIRE

E. C. SPOONER

E. V. VORLICK

Photolithographic Reproductions

By Permission of The American Chemical Society

JOHNSON REPRINT CORPORATION  
New York, N. Y. U. S. A.



THE JOURNAL

—OF THE—

AMERICAN CHEMICAL SOCIETY.

---

VOLUME XXIV.

1902.

---

COMMITTEE ON PAPERS AND PUBLICATIONS:

WILLIAM A. NOYES, Editor.	EDWARD HART,
W. F. HILLEBRAND,	J. H. LONG,
WM. MCMURTRIE,	ARTHUR A. NOYES,
EDGAR F. SMITH,	H. N. STOKES,
H. P. TALBOT, .	H. W. WILEY.

Photolithograph Reproduction  
By Permission of The American Chemical Society

JOHNSON REPRINT CORPORATION  
NEW YORK, N. Y., U. S. A.

2  
R 5.1 12 1



---

COPYRIGHT, 1902.

BY WILLIAM A. NOYES, EDWARD HART, W. F.  
HILLEBRAND, J. H. LONG, WM. MCMURTRIE,  
ARTHUR A. NOYES, EDGAR F. SMITH, H. N.  
STOKES, H. P. TALBOT, and H. W. WILEY.

Committee on Papers and Publications of the  
American Chemical Society.

---

PHOTOLITHOGRAPHED BY  
THE MURRAY PRINTING COMPANY  
WAKEFIELD, MASSACHUSETTS

## PAPERS.

### JANUARY.

Contribution to the Chemistry of <i>Stylophorum Diphyllum</i> . By J. O. Schlotterbeck and H. C. Watkins . . . . .	1
The Discovery of Nitroglycerine in an Exhumed Body. By G. G. Pond . . . . .	18
On the Production of the Imides of Succinic and Glutaric Acids by the Partial Hydration of the Corresponding Nitriles. By Marston Taylor Bogert and David C. Eccles . . . . .	20
On the Determination of Citrate-Insoluble Phosphoric Acid. By C. D. Harris . . . . .	25
A Hydrolytic Derivative of the Globulin Edestin and Its Relation to Weyl's Albuminate and the Histon Group. By Thomas B. Osborne . . . . .	28
The Basic Character of the Protein Molecule and the Reactions of Edestin with Definite Quantities of Acids and Alkalies. By Thomas B. Osborne . . . . .	39
A Study of the Available Mineral Plant Food in Soils. By C. C. Moore . . . . .	79
NEW BOOKS: Methods of Chemical Analysis and Foundry Chemistry . . . . .	116

### FEBRUARY.

The Development of Chemistry. By F. W. Clarke . . . . .	117
A Type of Reaction by which Sodium Carbonate and Hydrochloric Acid May Be Formed in the Animal Organism. By Thomas B. Osborne . . . . .	138
Sulphur in Protein Bodies. By Thomas B. Osborne . . . . .	140
The Peroxide Calorimeter as Applied to European Coals and Petroleum. By S. W. Parr . . . . .	167
Studies in Nitrification. By J. G. Lipman . . . . .	171
Rapid Method for the Volumetric Determination of Molybdenum Steel. By Francis T. Kopp . . . . .	186
Tellurium Tetrachloride. By Victor Lenher . . . . .	188
Preliminary Communication upon Glucophosphoric Acid. By P. A. Levene . . . . .	190
NEW BOOKS: <i>Analyse des Engrais</i> ; A Short Manual of Inorganic Chemistry; Chemical Lecture Experiments; Research Papers from the Kent Chemical Laboratory of Yale University; American Handy-Book of the Brewing, Malting, and Auxiliary Trades; Handbook on Sanitation; <i>Leitfaden für den Unterricht in der anorganischen Chemie</i> ; Subject List of Works on Chemistry and Chemical Technology in the Library of the British Patent Office; Smokeless Powder, Nitrocellulose, and the Theory of the Cellulose Molecule; A Compendium of Gold Metallurgy and Digest of U. S. Mining Laws, Water Rights, and Desert Land Laws . . . . .	192
Books Received . . . . .	200

## MARCH.

Ninth Annual Report of the Committee on Atomic Weights. Determinations Published in 1902. By F. W. Clarke . . . . .	201
Metallic Soaps from Linseed Oil. An Investigation of Their Solubilities in Certain of the Hydrocarbons. By Hermann T. Vulté and Harriet Winfield Gibson . . . . .	215
On the Decomposition of Sodium Nitrate by Sulphuric Acid. By C. W. Volney . . . . .	222
On the Ferrocyanides of Cadmium. By Edmund H. Miller . . . . .	226
Proximate Analysis of Spent Alkaline Liquor from the Reduction of Poplar Wood for Paper Stock, by the Soda Process, with a Description of the Method. By Martin L. Griffin . . . . .	235
Does "Argemone Mexicana" Contain Morphine? By J. O. Schlotterbeck . . . . .	238
Determination of Manganese in Iron. By William A. Noyes and G. Harry Clay . . . . .	243
New Apparatus. By Charles B. Williams . . . . .	246
A Rotary Cement Kiln for Use in the Laboratory. By E. D. Campbell . . . . .	248
The Alloys of Aluminum. By William Campbell and John A. Mathews . . . . .	253
On the Temperature Reaction of Oils with Sulphuric Acid—Maumené's Test. By H. C. Sherman, J. L. Danziger, and L. Kohnstamm . . . . .	266
A Note on the Determination of Molybdenum in Steel. By George Auchy . . . . .	273
Preliminary Note on a New Separation of Thorium. By Floyd J. Metzger . . . . .	275
NOTE: Reinsch's Test for Arsenic . . . . .	276
NEW BOOKS: On the Composition of Dutch Butter; The Manufacture of Alum and the Sulphates and Other Salts of Alumina and Iron; Vorlesungen über theoretische und physikalische Chemie; The Chemical Essays of Charles William Scheele; Annuaire pour l'an 1902, publié par le Bureau des Longitudes; The Dyeing of Cotton Fabrics; Modern Chemistry; Induction Coils; Lectures on the History of the Development of Chemistry since the Time of Lavoisier; Experiments on Losses in Cooking Meats; The Practical Methods of Organic Chemistry; Logarithms of Numbers and Chemical Factors; An Introduction to Chemical Analysis, for Students of Medicine, Pharmacy, and Dentistry; Methods for the Analysis of Ores, Pig Iron, and Steel; Les Carbures d'Hydrogène, 1851-1901; The Elements of Qualitative Analysis; The Laboratory Companion to Fats and Oils Industries . . . . .	277
Books Received . . . . .	294

## APRIL.

On the Inhibition of Chemical Reactions by Foreign Substances. I. By S. W. Young . . . . .	297
The Action of Methyl and Ethyl Alcohols upon the Bromides of Certain Propenyl Compounds. By F. J. Pond, E. S. Erb, and A. G. Ford . . . . .	327
The Determination of Sulphur in Plants. By G. S. Fraps . . . . .	346

On the Relation of the Heat of Combustion to the Specific Gravity in Fatty Oils. By H. C. Sherman and J. F. Snell . . . . .	348
Action of Selenic Acid on Gold. By Victor Lenher . . . . .	354
Naturally Occurring Telluride of Gold. By Victor Lenher . . . . .	355
Some Compounds of Pyridine. By J. Arthur Hayes . . . . .	360
Common Errors in the Determination of Silica. By W. F. Hillebrand . . . . .	362
A Redetermination of the Atomic Weight of Calcium—Preliminary Paper. By Theodore William Richards . . . . .	374
Commercial Aqua Ammonia, Its Effect upon Iron, Its Impurities, and Methods for Determining Them. By J. D. Pennock and D. A. Morton . . . . .	377
A Nitrogen Apparatus. By J. A. Wesener . . . . .	388
A New Form of Alkalimeter. By Charles B. Davis . . . . .	391
The Determination of Lithia in Lepidolite. By W. J. Schieffelin and W. R. Lamar . . . . .	392
A Note on the Use of the Bechi or Silver Nitrate Test on Olive Oils. By L. M. Tolman . . . . .	396
A Study of the Bechi Test for Cottonseed Oil. By Augustus H. Gill and Charles H. Dennison . . . . .	397
NEW BOOKS : Studies from the Chemical Laboratory of Sheffield Scientific School . . . . .	398

## MAY.

Contributions to the Chemistry of the Rare Earths of the Yttrium Group. I. By L. M. Dennis and Benton Dales . . . . .	401
Electrolytic Deposition of Lead from a Phosphoric Acid Solution. By A. F. Linn . . . . .	435
Researches on Thiocyanates and Isothiocyanates. By Henry L. Wheeler and Henry F. Merriam . . . . .	439
Liquid Mixtures of Minimum Boiling-Point. By Clifford D. Holley . . . . .	448
The Volumetric Estimation of Alumina, and Free and Combined Sulphuric Acid in Alums. By Alfred H. White . . . . .	457
The Analytical Constants of Neatsfoot, Tallow, and Horse Oils. By Augustus H. Gill and Allan W. Rowe . . . . .	466
A Test for the Gumming Quality of Lubricating Oils. By Augustus H. Gill . . . . .	467
Analyses Required for an Electrolytic Alkali Works. By J. H. James and J. C. Ritchey . . . . .	469
Burette Arrangement. By E. M. Johnson . . . . .	476
A Generator for Hydrogen Sulphide. By J. N. Swan . . . . .	476
The Determination of Copper by Aluminum Foil. By Geo. E. Perkins . . . . .	478
Supplementary Note to a "Gravimetric Method for the Estimation of Hydrogen Dioxide." By George E. Hosch . . . . .	479
NEW BOOKS : Elementary Electricity and Magnetism ; Enzymes and Their Application ; Reprints of Science Classics No. 1 ; Studien zur Kenntniss der Abhängigkeit der Viscosität der flüssigen Körper von der Temperature und von ihrer chemischen Constitution ; The Ex-	

perimental Study of Gases; The Manufacture of Paint; Leçons sur la Theorie des Gaz ; The Manufacture of Mineral and Lake Pigments ; The Elements of Physical Chemistry ; Drying Oils, Boiled Oils, and Solid and Liquid Dryers . . . . .	480
--	-----

## JUNE.

The Atomic Weight of Arsenic. By W. Clarence Ebaugh . . . . .	489
Lecture Experiments Illustrating Various Types of Catalytic Action. By A. A. Noyes and G. V. Sammet . . . . .	498
The Polarization of Fruits, Jellies, Jams, and Honies. By L. M. Tolman . . . . .	515
The Substitution of Hydrogen for Chlorine in Trichlormethylparaconic Acid. By Henry C. Myers . . . . .	525
Nitrification in Different Soils. By W. A. Withers and G. S. Fraps . . . . .	528
New Apparatus in Water Analysis. By George Edward Thomas and Clarence A. Hall . . . . .	535
Aromatic Bases as Precipitants for Rare Earth Metals. By Alice Mac-Michael Jefferson . . . . .	540
A New Method for the Approximate Determination of Uric Acid in Urine. By Julius Rudisch and Leopold Boroschek. . . . .	562
Lead Thiocyanate. By R. D. Hall . . . . .	570
Ammonium Vanadicophosphotungstate. By Edgar F. Smith and Franz F. Exner . . . . .	573
A New Qualitative Test for Cobalt. By J. L. Danziger . . . . .	578
A Note on the Volumetric Determination of Copper. By S. W. Parr . . . . .	580
The American Electrochemical Society. By Joseph W. Richards . . . . .	581
NEW BOOKS: The Letters of Jöns Jakob Berzelius and Christian Friederich Schönbein, 1836-1847; A Travers la Matière et l' Energie; Sewage and the Bacterial Treatment of Sewage; The Elements of Physical Chemistry; American Standard Specifications for Steel; Grundzüge der Siderologie; A Laboratory Guide in Elementary Bacteriology . . . . .	584

## JULY.

On Trivalent Carbon. By M. Gomberg . . . . .	597
The Ammonium Tungstates. By Thomas M. Taylor . . . . .	629
The Application of Eschka's Method to Pig Irons. By John V. R. Stehman . . . . .	644
The Constitution of Camphene. By F. D. Dodge . . . . .	649
Determination of Sulphuric Acid in Soils. By C. B. Williams . . . . .	658
The Interaction of Sulphuretted Hydrogen and Arsenic Acid. By L. W. McCay . . . . .	661
The Solubility of Gypsum. By George A. Hulett and Lucius E. Allen . . . . .	667
Researches on Thiocyanates and Isothiocyanates. By Henry L. Wheeler and Treat B. Johnson . . . . .	680
NOTES: Notes upon the Constants of Some Little Known Oils . . . . .	691
NEW BOOKS: Water Supply; Notes on Lead Ores; Gas and Fuel Analysis for Engineers; The American Yearbook of Medicine and	



Surgery for 1902; Indicators and Test-Papers; A Text-Book of Inorganic Chemistry; A Bibliography of the Analytical Chemistry of Manganese; Jahrbuch des Vereins des Spiritus-Fabrikanten in Deutschland, des Vereins der Stärke-Interessenten in Deutschland und der Brennerei-Berufsgenossenschaft; A Laboratory Manual of Physics for Use in High Schools; Plattner's Manual of Qualitative and Quantitative Analysis with the Blowpipe; Ammonia and Its Compounds—Their Manufacture and Uses . . . . .	691
---	-----

## AUGUST.

The Lake Superior Fire Assay for Copper. By George L. Heath . . . . .	699
Notes on the Estimation of Copper by Potassium Permanganate. By H. A. Guess . . . . .	708
The Influence of the Growth of Mold upon the Chemical Composition of Oleomargarine and Butter. By Charles A. Crampton . . . . .	711
An Electrolytic Study of Pyrroacemic Acid. By George W. Rockwell . . . . .	719
The Significance of Phosphates in Natural Waters. By A. G. Woodman . . . . .	735
Researches on Thiocyanates and Isothiocyanates. By Henry L. Wheeler and George S. Jamieson . . . . .	743
Refractive Indices of Salad Oils—Correction for Temperature. By L. M. Tolman and L. S. Munson . . . . .	754
The Production of Acylamines by the Interaction of Sodium Salts of Monobasic Acids and Amine Hydrochlorides. By Frederick L. Dunlap . . . . .	758
An Investigation of Wood Tar from the Douglas Fir; <i>Pseudotsuga Taxifolia</i> . By H. G. Byers and Paul Hopkins . . . . .	771
Investigation of the Oil of the Red Elderberry, <i>Sambucus Racemosa Arborescens</i> . By H. G. Byers and Paul Hopkins . . . . .	671
A Volumetric Method for the Estimation of Sulphuric Acid in Soluble Sulphates. By Yasujuro Nikaido . . . . .	774
A Preliminary Note on the Oil of Milfoil. By A. B. Aubert . . . . .	778
NEW BOOKS: Thermodynamique; Refrigeration, Cold Storage and Ice-Making; Modern Chemistry, with Its Practical Applications . . . . .	780

## SEPTEMBER.

Studies in Denitrification. By E. B. Voorhees . . . . .	785
On the Composition of the Ferrocyanides of Zinc. By Edmund H. Miller and J. L. Danziger . . . . .	823
On Standard Tartar Emetic and Its Structural Formula. By F. E. Hale . . . . .	828
Photometric Determination of Iron. By J. I. D. Hinds and Myrtis Louise Cullum . . . . .	848
On the Determination of Sulphur in Coal. By Charles W. Stoddart . . . . .	852
On a Method for the Determination of Very Small Vapor-Tensions in Certain Circumstances. By Launcelot W. Andrews . . . . .	864
Contributions to the Study of Starch Iodide. By Launcelot W. Andrews and Henry Max Goettsch . . . . .	865
A Thermochemical Constant. By F. W. Clarke . . . . .	882

A New Glass for Low Solubility. By. G. E. Barton . . . . .	893
NOTES: Rapid Volumetric Method for Determining Phosphoric Acid in Fertilizers; New Apparatus in Water Analysis . . . . .	895
NEW BOOKS: Grundriss der Qualitativen Analyse vom Standpunkte der Lehre von den Ionen . . . . .	898

## OCTOBER.

A New Separation of Thorium from Cerium, Lanthanum, and Didym- ium, and Its Application to the Analysis of Monazite. By Floyd J. Metzger . . . . .	901
Action of Tellurium and Selenium on Gold and Silver Salts. By R. D. Hall and Victor Lenher . . . . .	918
The Application of Polarimetry to the Estimation of Tartaric Acid in Commercial Products. By Edgar B. Kenrick and Frank B. Kenrick . . . . .	928
The Equivalent Conductivity of the Hydrogen Ion Derived from Transference Experiments with Hydrochloric Acid. By A. A. Noyes and G. V. Sammet . . . . .	944
Some Preliminary Experiments upon the Clinkering of Portland Cement. By E. D. Campbell . . . . .	969
On the Quantitative Separation of Maltose and Lactose. By Charles I. Boyden . . . . .	993
On the Electrical Conductivity of Urine in Relation to Its Chemical Composition. By J. H. Long . . . . .	996
The Retention of Arsenic by Iron in the Marsh-Berzelius Method. By Charles Lathrop Parsons and Morris A. Stewart . . . . .	1005
On the Constitution of Certain Organic Salts of Nickel and Cobalt as They Exist in Aqueous Solution. By O. F. Tower . . . . .	1012
On the Manganese Ferrocyanides. By Albert Ernest Dickie . . . . .	1023
NOTES: Note on the Preparation of Metallic Lithium; A Novel Con- stant High Temperature Bath; On an Adulteration of Lavender Oil with Salicylic Acid; The Production of Acylamines by the Interaction of Sodium Salts of Monobasic Acids and Amine Hydro- chlorides . . . . .	1024

## NOVEMBER.

The Synthesis of Alkylketodihydroquinazolines from Anthranilic Ni- trile. By Marston Taylor Bogert and William Flowers Hand . . . . .	1031
The Action of Iso-Valeric Aldehyde upon Antipyrine. By David C. Eccles . . . . .	1050
On the Reduction of Some Aromatic Nitro-Compounds. By F. J. Al- way and M. D. Welsh . . . . .	1052
On the Nitration of Benzyl Chloride. By Frederick J. Alway . . . . .	1060
Condensation of Chloral with the Nitrilanines. By Alvin S. Wheeler and H. R. Weller . . . . .	1063
Preparation of 2,5-Dimethylbenzyl-2,5-Dimethylbenzal Hydrazone and its Benzoyl and Acetyl Derivatives. By Everhart Percy Harding and Edgar W. Rice . . . . .	1066

Preparation of 2,4,6-Trimethylbenzaldazine ; of 2,4,6-Trimethylbenzyl-2,4,6-Trimethylbenzal Hydrazone and Some of its Derivatives. By Everhart Percy Harding . . . . .	1068
Arsenic Pentachloride. By Charles Baskerville and H. H. Bennett . . . . .	1070
Observations on the Electrolytic Precipitation of Zinc and of Copper. By Edgar F. Smith . . . . .	1073
The Use of Potassium-Ferric Chloride for the Solution of Steel in Making the Determination of Carbon. By Geo. Wm. Sargent . . . . .	1076
An Automatic Gas-Generator. By Henry H. Denham . . . . .	1080
The Copper Assay by the Iodide Method. By Albert H. Low . . . . .	1082
The Quantitative Determination of Selenium in Organic Compounds. By R. E. Lyons and F. L. Shinn . . . . .	1087
The Determination of Sulphur and Phosphorus in Plant Substances. By C. P. Beistle . . . . .	1093
The Determination of Sulphur and Phosphorus in Organic Materials. By H. C. Sherman . . . . .	1100
Further Notes on the Bromine Absorption of Oils. By Parker C. McIlhenny . . . . .	1109
Fixation of Phosphoric Acid in the Soil. By J. T. Crawley . . . . .	1114
The Estimation of Soil Acidity and the Lime Requirements of Soils. By F. P. Veitch . . . . .	1120
The Analysis of Vanilla Extract. By A. L. Winton and M. Silverman . . . . .	1128
Creaming of Milk During Its Sale. By William Frear and M. H. Pingree . . . . .	1136
NEW BOOKS : On Cane-Sugar and the Process of Its Manufacture in Java ; The Gas Engineer's Laboratory Handbook ; Guide to Preparation Work in Inorganic Chemistry . . . . .	1138

## DECEMBER.

The Solubility Equilibrium between Silver Chloride, Silver Oxide, and Solutions of Potassium Chloride and Hydroxide. By A. A. Noyes and D. A. Kohr . . . . .	1141
Some Notes Concerning Halphen's Test for Cottonseed Oil. By Elton Fulmer . . . . .	1148
Fixation of Atmospheric Nitrogen by Alfafa on Ordinary Prairie Soil under Various Treatments. By Cyril G. Hopkins . . . . .	1155
The Identification and Composition of Malt Liquors. By Charles Lathrop Parsons . . . . .	1170
On Azoxybenzene. By Arthur Lachman . . . . .	1178
Derivatives of Phenylether. III. By Alfred N. Cook and Charles F. Eberly . . . . .	1200
The Determination of Manganese in Iron and Steel. By John V. R. Stehman . . . . .	1204
The Rapid Determination of Carbon by Combustion. By George Auchy . . . . .	1206
NORRIS : Filtration and Determination of Crude Fiber ; A Rapid Method for Separating Zinc and the Alkaline Metals from Iron . . . . .	1211

NEW BOOKS : The Mineral Industry : Its Statistics, Technology, and Trade in the United States and Other Countries to the End of 1901 ; Inorganic Chemistry, with the Elements of Physical and Theoretical Chemistry ; Acht Vorträge über physikalische Chemie ; The Chemistry of the Terpenes ; Handbook of Technical Gas Analysis ; Methods of Gas Analysis ; Sewage Works Analyses ; Congrès International d' Electricité, Paris, 1900 . . . . .	1210
--	------

# THE JOURNAL

OF THE

## AMERICAN CHEMICAL SOCIETY.

---

### CONTRIBUTION TO THE CHEMISTRY OF *STYLOPHORUM* *DIPHYLLUM*.

BY J. O. SCHLOTTERBECK AND H. C. WATKINS.<sup>1</sup>

Received October 2, 1901.

*STYLOPHORUM diphylum*, which is popularly known by the suggestive names yellow poppy and celandine poppy, belongs to the *Papaveraceae*. It grows in low woods from Ohio to Tennessee and westward to Wisconsin and Missouri. It is a perennial, herbaceous plant, with leaves pinnatifid in a manner similar to celandine. The flowers are deep yellow, poppy-like, and about an inch broad. The fruits are ovoid and tipped with the persistent style; hence, the generic name *Stylophorum*. All parts of the plant exude a yellow juice, when bruised, which matches the color of the corolla. Under the name extra "large golden seal" the root is mentioned<sup>2</sup> as a possible accidental admixture of *hydrastis*.

Undoubtedly J. U. Lloyd was the first to undertake a chemical examination of this plant, but we have not been able to locate the account of his results. In a letter to us he writes that some twenty years ago his brother, C. G. Lloyd, called his attention to this plant and suggested that he make a chemical examination

<sup>1</sup> Holder of the F. Stearns & Co. Fellowship in the School of Pharmacy, University of Michigan.

<sup>2</sup> Lloyd: "Drugs and Medicines of North America," 1, 95.

for alkaloids, since its relationship, botanically, indicated their presence. Acting upon this suggestion, Mr. Lloyd extracted a considerable quantity of the root and obtained a large alkaloidal product which he provisionally named stylophorine in order that it might have a place in literature. This product was sent to Professor Eykman, of Tokio, Japan, for critical study since he was at that time especially engaged in studying the constituents of the *Papaveraceae*. We have also failed to find in literature a report by this chemist upon *Stylophorum* or its alkaloids, but that he did concern himself with this subject is shown in an article by Schmidt<sup>1</sup> upon our plant in which he states that the results communicated by Ekyman agreed with his own. These two chemists believe that the principal alkaloid of *Stylophorum diphyllum*, and chelidonine of *Chelidonium majus* are identical.

A comparative examination of stylophorine<sup>2</sup> and chelidonine was made by Schmidt and Selle<sup>3</sup> in 1890. The identity was fully established and in addition they obtained evidence of the existence of two other alkaloids, but the isolation was not made because of scarcity of material. This is probably the extent of the work done on this plant at the time it was taken up by the authors.

Through the kindness of Professor Lloyd we were supplied with 50 pounds of the dried root which was collected by a professional root digger in the woods northeast of Cincinnati, Ohio. Quoting from his letter to us Mr. Lloyd says: "The *Stylophorum* has been collected and worked with the utmost care and no foreign substance is present in it. It was inspected piece by piece and you can use it with confidence."

#### METHOD OF EXTRACTION.

The drug in No. 20 powder was first thoroughly moistened with about 5 per cent. ammonia water for the purpose of liberating the bases from the acids with which they were combined in the plant, and then spread out in thin layers to dry at ordinary temperature. For the extraction a copper apparatus based upon the Soxhlet principle and of about 25 pounds' capacity was employed. Chloroform was the solvent used and extraction was continued until a portion of the liquid drawn from the bottom of the percolator did not, after the usual manipulation, respond to the

<sup>1</sup> *Arch. d. Pharm.*, 226, 622.

<sup>2</sup> While Lloyd applied the name stylophorine to the entire alkaloidal product, Schmidt, Selle, Eykman and others employed it specifically to the most abundant alkaloid.

<sup>3</sup> *Arch. d. Pharm.*, 228, 96.

test for alkaloids. The chloroform was recovered from the percolate and the waxy, dark-colored residue repeatedly digested with acidulated (acetic acid) water upon the steam-bath until exhausted of its alkaloid. The combined reddish, transparent filtrates contained the total alkaloids as acetates.

The chloroform held by the marc was entirely recovered by passing high pressure steam in at the bottom of the percolator, condensing the mixed vapors of water and chloroform, and separating the two layers. The hot marc was at once percolated with distilled water for the purpose of extracting the soluble salts naturally existing in the drug as well as the ammonium salts of the acids originally combined with the bases. The aqueous percolate was concentrated to small volume, 10 per cent. of alcohol added for preservation, and set aside for later study.

The red solution of the acetates of the bases was made alkaline with ammonia water whereupon a very bulky, grayish precipitate was thrown down. This was collected on a large Buchner filter and thoroughly washed with water. The filtrate was now golden yellow in color instead of red, thus showing that the red color body is precipitated with ammonia. This indicates the presence of a base allied to the red salt-forming alkaloid of *Sanguinaria*, *Chelidonium*, and *Bocconia*. The yellow color of the filtrate also indicates the presence of a color body other than the yellow salt-forming alkaloid found in the allied plants. The yellow filtrate, as well as all filtrates from similar operations as long as they possessed considerable color, was reserved and worked later for the coloring-matter.

The alkaloids were redissolved in a small amount of glacial acetic acid to the usual bright red solution, diluted with water, reprecipitated with ammonia, and washed as before. This operation for preliminary purification was repeated a number of times until the precipitate was nearly white.

#### ISOLATION OF THE ALKALOIDS.

Successive convenient portions of the alkaloid were dissolved in acid, placed in a separator, about an equal volume of ether added and then ammonia to alkaline reaction. If not too much alkaloid be taken, a moment's vigorous shaking causes complete solution of the bases in the ether, which takes on a bluish fluorescence. Solution is only temporary, however, so that separation and filtration through a tuft of cotton must be made rapidly, to

avoid premature crystallization. We have found wide-mouthed Erlenmeyer flasks of different sizes admirably suited for crystallizing since undue loss of ether is avoided and the alkaloid does not creep up the side of the dish. Generally the alkaloid begins to separate from the filtered solution in a very short time and sometimes even before it can be drawn from the separator. After no visible increase in crystallization takes place (generally after several hours), the supernatant ethereal solution, if it be practically colorless, is at once used again to shake out another portion of alkaloid, but if it be colored the ether is recovered by distillation, dried, and then used over again. If after several hours' standing no crystals separated from a colorless or nearly colorless solution, it was concentrated to small volume and again set aside to crystallize. The entire alkaloid was treated in this manner and all the filters and cotton plugs thrown into a waste jar for later recovery. The strictest economy was observed with the alkaloids, so we can say that practically none was lost.

It was noticed that crystals of two distinct forms would separate, sometimes both together, sometimes one form alone, and then again the other. The predominating alkaloid separated in the form of monoclinic prisms (Fig. 1), while the second crystallized in needles (Fig. 2). By close watching, these two forms could be completely separated by fractional crystallization. The different fractions of the former alkaloid melted from  $130^{\circ}$ – $134^{\circ}$  and of the latter from  $197^{\circ}$ – $200^{\circ}$ , both of course in the unpurified state.

By a continuous repetition of the above process of dissolving in acetic acid, precipitating with ammonia and shaking out with ether extending over a period of fully three months, the entire alkaloidal product was worked up. All fractions of the prisms were united as well as those of the needles.

A very interesting and peculiar property of the principal alkaloid, which we shall see later is identical with chelidonine, was accidentally discovered while scraping a large fraction of crystals from the sides of the crystallizing flask with a glass rod. As the rod rubbed against the crystals the faces seemed to reflect light to an unusual extent; consequently, the phenomenon of "triboluminescence"<sup>1</sup> suggested itself. The experiment was repeated in a perfectly dark room with greater success, an intense light being

<sup>1</sup> *Ann. Phys. (Wied.)*, **34**, 446; *Ber. d. chem. Ges.*, **34**, 1820.



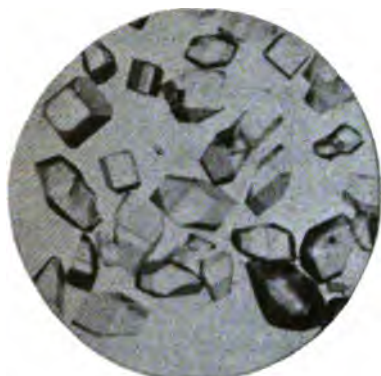


Fig. 1.—Chelidonine.  
 $C_{20}H_{19}NO_5 \cdot H_2O$

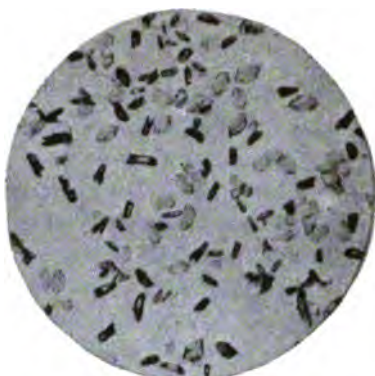


Fig. 2.—Chelidonine Hydrochloride.  
 $C_{20}H_{19}NO_5 \cdot HCl$

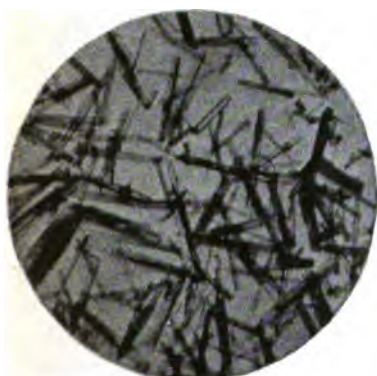


Fig. 3.—Stylopine.  
 $C_{19}H_{19}NO_5$

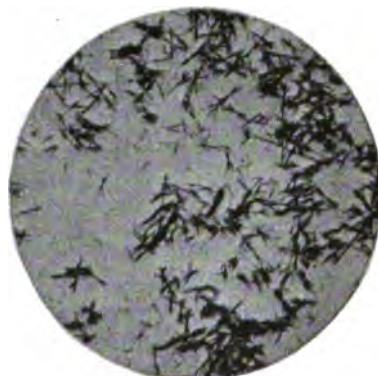


Fig. 4.—Stylopine Hydrochloride.  
 $C_{19}H_{19}NO_5 \cdot HCl$



Fig. 5.—Protopine.  
 $C_{20}H_{19}NO_5$

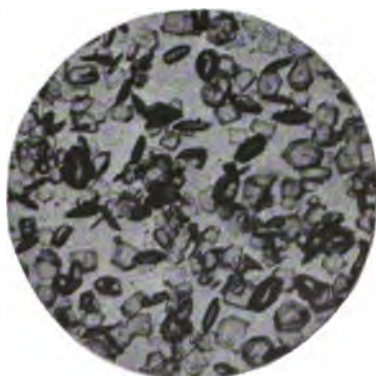


Fig. 6.—Diphylline.



emitted as the crystals were crushed. This is in some way connected with the crackling or snapping sound which we often heard coming from flasks in which very active crystallization was taking place. Whether an actual break in the crystals took place we cannot say. A solution in which an active growth of crystals was taking place was set in a dark room and watched for some time. Each crackling sound spoken of was accompanied by a feeble spark. When a flask containing large crystals was placed in the palm of the hand, the body heat was sufficient to produce the sound as well as the light. The same result was obtained when a flask of crystals was given a rotary motion. If a flask containing dry crystals be moderately shaken, the impact of the crystals against the side of the flask produced hundreds of intensely bluish white, scintillating sparks. These were best obtained with dry crystals from ether, not so well with those from chloroform or alcohol, or from mixtures of them. Covered with water, ether, or benzene the effect is produced equally well. By shaking a flask of dry crystals close to the face of a sensitive plate covered by a negative, a positive was obtained with a very short exposure. Other experiments are under way and will be reported upon later, but we are of the opinion that electricity of cleavage is the phenomenon manifested. Since of all the alkaloids of *Stylophorum* this one alone possessed this feature, it served as an excellent identifying characteristic in the isolation.

In the later mother ethereal liquids, three other alkaloids were separated by a very tedious and monotonous routine of fractional crystallization. These five alkaloids, all of which were obtained by the above method of isolation with ether as a solvent, we shall designate by the numerals I, II, III, IV, V. Alkaloid V was the last to be isolated because of its extreme solubility in ether, but its identity was practically established early in the process as was stated above.

#### ALKALOID I.

By far the greater portion of the total basic product consists of this alkaloid. Purification was effected as follows: The total product was dissolved in dilute sulphuric acid and treated with an excess of strong hydrochloric acid. The salt began to separate in a very short time in the form of a coarsely crystalline powder. After collecting on a filter it was dissolved in boiling water, rapidly filtered through a tuft of cotton, the solution cooled with

ice-water and stirred to granulation. This was repeated at least ten times or until the hydrochloride became white. The combined filtrates were treated in a similar manner. A portion of the hydrochloride dissolved in water, converted into a free base and shaken out with ether, soon yielded crystals that melted at  $136^{\circ}$  (uncorr.). The remainder of the salt was so treated, and then recrystallized several times from hot alcohol and finally from a mixture of chloroform and alcohol. From the latter mixture large crystals fully  $\frac{1}{4}$ -inch long were easily obtained which melted at exactly the same point as before. From its melting-point, crystalline form, and behavior with solvents there is no question in our minds that this, the principal alkaloid of *Stylophorum*, is chelidonine.

Chelidonine has as yet been found in only one other plant, viz., *Chelidonium majus*. It was first isolated by Godefroy<sup>1</sup> but in an impure state. Probst<sup>2</sup> was the first to obtain it pure and to study some of its properties. At about the same time Reuling<sup>3</sup> published a short article upon this base but he did not add much to the existing knowledge. A few years later Polex<sup>4</sup> concerned himself with the alkaloid and obtained it pure. Eykman<sup>5</sup> contributed an article upon chelidonine but it was separated from *Chelidonium majus* and not from *Stylophorum diphyllum*. He did not arrive at definite conclusions regarding the composition, however. Henschke<sup>6</sup> made a close study of chelidonine, likewise from *Chelidonium*. Schmidt and Selle<sup>7</sup> are the only ones who have published accounts of work done upon the alkaloids from *Stylophorum*.

There exists in literature considerable discrepancy regarding the composition of this alkaloid. Will<sup>8</sup> made combustions and calculated the formula  $C_{40}H_{40}N_2O_8$  an expression that was variously interpreted as follows: Gerhardt<sup>9</sup>  $C_{40}H_{19}N_2O_8$ , Gmelin<sup>10</sup>  $C_{42}H_{19}N_2O_8$ , Löwig<sup>11</sup>  $C_{40}H_{20}N_2O_8$ , Limpricht<sup>12</sup>  $C_{19}H_{17}N_2O_8$ . Henschke, and Schmidt and Selle succeeded in obtaining concordant results and

<sup>1</sup> *J. de Pharm.*, Dec., 1824.

<sup>2</sup> *Ann. Chem. (Liebig)*, **29**, 113.

<sup>3</sup> *Ibid.*, **29**, 131.

<sup>4</sup> *Arch. d. Pharm.*, **16**, 77.

<sup>5</sup> *Rec. trav. chim. Pays-Bas*, **3**, 190.

<sup>6</sup> *Arch. d. Pharm.*, **226**, 624.

<sup>7</sup> *Ibid.*, **228**, 96.

<sup>8</sup> *Ann. Chem. (Liebig)*, **38**, 113.

<sup>9</sup> *Traité* **4**, 210.

<sup>10</sup> *Handbuch*, IV, 1534.

<sup>11</sup> *Lehrbuch*, 1846.

<sup>12</sup> *Lehrbuch*, 1862.

the formula  $C_{30}H_{19}NO_5 \cdot H_2O$ . We believe that much of the difficulty encountered in the determination of the composition of this base rests in the fact that purification is effected with difficulty.

Having prepared a considerable quantity of chelidonine from *Stylophorum*, we took up its study mainly for the purpose of verifying the very latest results upon its composition.

For the determination of water of crystallization a small quantity of the freshly crystallized alkaloid was heated in an air-bath at a temperature of  $100^\circ$  to constant weight. Henschke used heat of  $125^\circ C.$ , but at this temperature our product became gradually darker. Since neither Henschke nor Selle make mention of this in their report we were of the impression that our product must still be contaminated with impurities, therefore, the colorless alkaloid was recrystallized twice from alcohol and again heated but with the same result. Then a lower heat was tried and sufficiently prolonged to cause an appreciable loss of water, but again with the same change in color. Fearing that this coloration indicated a slight decomposition and therefore would vitiate results, an attempt was made to remove the water in a vacuum desiccator over sulphuric acid and phosphoric anhydride until the substance lost no weight.

A vacuum was maintained (with interruptions for weighing) for fully a month and it was noticed as increasing quantities of water were removed the alkaloid became more yellow. Unfortunately we could not complete the experiment because of an accident but it was plainly evident that with removal of water of crystallization even in the cold, discoloration takes place. Since light seems to hasten the change, there is in progress at this time an experiment to determine whether all the water is removed and also whether discoloration takes place in the dark.

A sample heated to constant weight at  $100^\circ$  for about fourteen hours lost 4.5 per cent. of its weight. According to the formula  $C_{30}H_{19}NO_5 \cdot H_2O$ , the theoretical amount of water is 4.8 per cent.

Several combustions were made with the air-dried material as well as with that dried to constant weight but the results were not as concordant as was desired and were therefore rejected. Excellent results were obtained with the nitrate which is easily made pure and which contains no water of crystallization. In the estimation of the acid in the hydrochloride by means of silver nitrate the filtrate from the precipitated silver chloride separated

large needles of the nitrate of chelidonine. After recrystallizing several times from hot water and drying in a desiccator, the following results of the combustions were obtained :

I. 0.333 gram chelidonine nitrate gave 0.7044 gram carbon dioxide and 0.1524 gram water.

II. 0.350 gram chelidonine nitrate gave 0.1532 gram water.

III. 0.317 gram chelidonine nitrate gave 0.6738 gram carbon dioxide and 0.1354 gram water.

	Calculated for $C_{20}H_{19}NO_5 \cdot HNO_3$ .	I.	Found. II.	III.
Carbon.....	57.69	57.69	....	57.63
Hydrogen.....	4.84	5.08	4.86	4.74

Nitrogen was determined by the Dumas as well as by the Kjeldahl method. By the former method the following results were obtained :

I. 0.4926 gram of anhydrous chelidonine gave 0.0211 gram of nitrogen, or 4.27 per cent.

II. 0.551 gram of anhydrous chelidonine gave 0.022 gram of nitrogen, or 3.97 per cent.

Theory requires 3.96 per cent.

By the latter method the following results were obtained :

I. 0.412 gram of chelidonine gave 3.33 per cent. of nitrogen.

II. 0.486 gram of chelidonine gave 3.40 per cent. of nitrogen.

Theory requires 3.77 per cent.

The hydrochloride was prepared and purified as stated above. Air-dried material heated in an oven for several hours did not lose weight; therefore there is no water of crystallization. The acid was determined in the customary way with silver nitrate and weighing the washed and dried silver chloride.

I. 0.455 gram of chelidonine hydrochloride gave 0.1656 gram silver chloride.

II. 0.3406 gram of chelidonine hydrochloride gave 0.1264 gram silver chloride.

	Calculated for $C_{20}H_{19}NO_5 \cdot HCl$ .	I.	Found. II.
Hydrochloric acid.....	9.36	9.22	9.4

The analyses of the gold and platinum double salts verified the formula obtained from combustions of the nitrate. The gold salt was readily made by precipitating a hot acid solution of the hydrochloride of chelidonine with an excess of a 2 per cent. solution of gold chloride. The double salt separated as a voluminous, orange-red precipitate which was collected on a filter, thoroughly washed and dissolved in hot alcohol. Beautiful violet-red crystals bunched in rosettes separated in a short time and these were re-

crystallized and dried in a desiccator. Heating in an oven at  $100^{\circ}$  for several hours did not cause it to lose weight.

1. 0.0774 gram of the gold salt yielded, upon incineration, 0.022 gram gold.

	Calculated for $C_{20}H_{10}NO_3 \cdot HCl \cdot AuCl_3$	Found.
Gold.....	28.1	28.42

The platinum salt was made in the same manner, using a 5 per cent. solution of platinum chloride. The double salt separated as a yellowish precipitate which became denser and deeper colored when reprecipitated for purification. We did not succeed in obtaining crystals of this compound from ethyl or methyl alcohol. One small fraction that had been standing in methyl alcohol for several days had changed to fine silky needles but we were not able to repeat the operation. Heating to  $100^{\circ}$  to constant weight removes 3.4 per cent. water.

- I. 0.136 gram of the water-free double salt left, upon incineration, 0.0236 gram platinum.

	Calculated for $(C_{20}H_{10}NO_3 \cdot HCl)_2 \cdot PtCl_4 \cdot H_2O$	Found.
Platinum .....	17.45	17.4
Water.....	3.1	3.4

*Action of Ethyl Iodide.*—Five grams of pure dried material were heated in a bomb tube with an excess of pure ethyl iodide at  $130^{\circ}$ – $140^{\circ}$  for four hours. When cold, the tube was opened and only a slight pressure noticed. In the bottom of the tube there was an insoluble portion yellowish in color and above it a transparent, light red liquid. The excess of ethyl iodide was driven off and the residue dissolved in boiling alcohol. It was filtered and set aside in a small Erlenmeyer flask. While crystals began to appear after a considerable length of time we found that layering with an equal volume of ether as employed by Henschke hastened crystallization materially. Tufts of fine, silky needles formed on the side of the flask and at the contact zone of the two liquids. Successive crops were obtained and all the combined fractions recrystallized from the same solvents several times but with loss of considerable material. Enough was left, however, to determine the iodine content with silver nitrate. The new compound was found to be free of water of crystallization.

- I. 0.2038 gram of the compound gave 0.0948 gram silver iodide.

	Calculated for $C_{20}H_{10}NO_3 \cdot C_2H_5I$	Found.
Iodine .....	24.94	24.8

Long contact of potassium hydroxide with a solution of this compound had no effect since the same compound with identical melting-point was again obtained in almost quantitative amount. This alkaloid is probably a tertiary base, as was shown by Henschke.

For the determination of methoxyl groups a modification of Zeissel's well-known method was employed, using ground-glass joints throughout the entire apparatus. After carrying on the operation for fully an hour not the least turbidity was noticed in the silver nitrate solution. Methoxyl groups are therefore absent.

By pouring a solution of the sulphate of chelidonine into a large excess of Wagner's reagent, an abundant chocolate-colored precipitate formed which, upon shaking vigorously, became denser and settled to the bottom. The collected precipitate was thoroughly washed and then dissolved in hot methyl alcohol and set aside in flat crystallization dishes. Two distinct forms separated, one in light red needles and the other in almost black prisms. These were separated mechanically and each recrystallized several times from hot methyl alcohol. When dried in a desiccator and the iodine estimated with thiosulphate solution, the light red crystals gave figures that agree with the formula for the triiodide  $C_{20}H_{19}NO_3 \cdot HI \cdot I_3$ . The black prisms appear to have the formula  $C_{20}H_{19}NO_3 \cdot HI \cdot I_3$ .

Finally a solution of the free alkaloid chelidonine, dissolved in absolute alcohol, gave an optical rotation of  $[\alpha]_D = +115^{\circ}24'$ .

#### ALKALOID II.

This one is second in abundance and crystallizes in distinct needles as shown in Fig. 2. The needles which Selle obtained in such small quantity that only the melting-point ( $193^{\circ}$ – $195^{\circ}$ )<sup>1</sup> could be made are probably the same substance. Since we have not found in literature anywhere a description of an alkaloid possessing the properties of this one we have decided to designate it by the name stylopine. All the fractions of the needles melting in the neighborhood of  $200^{\circ}$  were united and purified in the same manner employed with chelidonine. A pure product was obtained that possessed the constant melting-point of  $202^{\circ}$  (uncorr.).

This alkaloid is almost insoluble in hydrochloric acid, forming fine needles of the salt when strong hydrochloric acid is added to a

<sup>1</sup> *Arch. d. Pharm.*, 228, 108.



solution of the acetate. It is also insoluble in dilute sulphuric acid which serves excellently as a means of separation from chelidonine. The free alkaloid is very soluble in glacial acetic acid, much less so in dilute acid. The nitrate separates from aqueous solutions in very small clusters of needles which in mass appear almost jelly-like, or gelatinous.

Precipitates were obtained with well-known reagents as follows :

Tannic acid.....	slight white.
Potassium bismuth iodide.....	light yellow flocculent.
Potassium cadmium iodide.....	white.
Bromine water.....	yellow.
Phosphotungstic acid.....	white.
Potassium iodide.....	white needles.
Phosphomolybdic acid.....	dirty white.
Gold chloride.....	salmon to yellow ochre.
Platinum chloride.....	white to pale yellow.
Picric acid.....	deep lemon yellow.
Potassium dichromate.....	yellow.
Wagner's reagent.....	chocolate-brown.

The free alkaloid contains no water of crystallization. Combustions of the pure dry substance gave the following results :

I. 0.1926 gram stylophine gave 0.4712 gram carbon dioxide and 0.0958 gram water.

II. 0.1718 gram stylophine gave 0.0864 gram water.

III. 0.1704 gram stylophine gave 0.4206 gram carbon dioxide and 0.0854 gram water.

IV. 0.2714 gram stylophine gave 0.6680 gram carbon dioxide.

Four nitrogen determinations gave the following results :

I. 0.1768 gram stylophine gave 0.007478 gram nitrogen.

II. 0.177 gram stylophine gave 0.007292 gram nitrogen.

III. 0.1824 gram stylophine gave 0.00698 gram nitrogen.

IV. 0.1316 gram stylophine gave 0.005578 gram nitrogen.

	Calculated for $C_{15}H_{19}NO_5$ .	Found.				Average.
		I.	II.	III.	IV.	
Carbon.....	66.83	66.72	....	66.78	67.1	66.86
Hydrogen ..	5.54	5.52	5.58	5.57	....	5.55
Nitrogen ...	4.10	4.23	4.12	3.83	4.24	4.10
Oxygen ....	23.46	....	....	....	....	23.49

The hydrochloride was made in the usual manner and purified by recrystallization from hot water. It contains no water of crystallization. For the determination of the formula of this salt the acid was estimated by precipitating with silver nitrate and weighing the washed and dried silver chloride. Only one estimation was made.

I. 0.0524 gram of the hydrochloride of stylopine gave 0.020 gram silver chloride or 9.7 per cent. hydrochloric acid.

	Calculated for $C_{19}H_{19}NO_3.HCl$ .	Found.
Hydrochloric acid.....	9.65	9.7

The platinum salt was made by precipitating a hot acid solution of the hydrochloride with a 5 per cent. solution of platinum chloride. The precipitate was light yellow at first but became darker after a second precipitation for purification. It contains no water of crystallization.

I. 0.0406 gram of the platinum salt gave, upon incineration, 0.0074 gram platinum.

II. 0.015 gram of the platinum salt gave, upon incineration, 0.0028 gram platinum.

	Calculated for $(C_{19}H_{19}NO_3.HCl)_2.PtCl_4$ .	Found.	
		I.	II.
Platinum.....	17.7	18.2	17.9

*Action of Ethyl Iodide.*—Two grams of the pure alkaloid were heated in a hard-glass tube with an excess of freshly prepared ethyl iodide at  $130^\circ$  for about two hours. Even in the cold the change begins to take place, but heating is required to complete it. The new compound in the tube became slightly yellow in color and was decidedly more voluminous than the original alkaloid. After cooling, the tube was opened and the excess of ethyl iodide removed by distillation. The residue was then dissolved in boiling alcohol and when cold layered with ether and set aside as before. The successive small crops were all united and again dissolved in alcohol and set aside as before. The new compound, consisting of small clusters of fine needles, melts at  $255^\circ$ . The iodine content of this compound was determined in the usual manner.

I. 0.1062 gram of the double salt gave 0.0486 gram silver iodide.

II. 0.1086 gram of the double salt gave 0.050 gram silver iodide.

	Calculated for $C_{19}H_{19}NO_3.C_2H_5I$ .	Found.	
		I.	II.
Iodine.....	25.5	24.7	24.8

Strong potassium hydroxide is absolutely without action upon this compound. We have here probably a tertiary base, although the proof is not completed.

A modification of Zeissel's method was employed for the determination of methoxyl groups but not the least turbidity was noticed in the silver nitrate solution; hence, we must conclude that these groups do not exist in this base.

For the determination of hydroxyl groups a small quantity was heated in a flask with acetic anhydride and sodium acetate under a reflux condenser for several hours. A slight change in color of the solution took place. When the liquid was poured into cold water many small, oily drops separated which, after a time, collected on the sides of the dish in the form of a varnish which possessed a disagreeable odor. Repeated trials to secure crystals from this varnish were without results and as the material was so small in quantity, we abandoned this part of the work until a larger quantity is available. Crystalline periodides are easily obtained by the usual method but here, too, because of scarcity of material, no analyses could be made.

Potassium iodide throws down a white precipitate of fine needles from a solution of stylophine in acetic acid. Not enough material was at hand to make duplicate determinations of the iodine but the probabilities are that the compound has the formula  $C_{18}H_{19}NO_5 \cdot HI$ .

The pure alkaloid dissolved in absolute alcohol rotates polarized light  $[\alpha]_D = -315^\circ 12'$ .

#### ALKALOID III.

This alkaloid is probably third in abundance in the plant but only a small portion was obtained from the original total product for the reason, as we shall see later, that it is to some extent soluble in ammonia. In the separation of the two alkaloids already described, this one made its appearance in only one or two fractions in an almost uncontaminated condition. Small white warts, and colorless transparent prisms were about equally abundant in these fractions. Protopine was at once suspected, and from the melting-point of  $203^\circ$  in the unpurified condition and its characteristic color reaction with sulphuric acid and Erdmann's reagent our suspicions were practically confirmed.

It will be recalled that the alkaline aqueous liquids that had been washed with ether for the removal of alkaloids were reserved as long as they possessed a yellow color. After acidulating this liquid with acetic acid and concentrating to smaller volume it was found that a curdy precipitate was thrown down with potassium hydroxide. This was shaken with ether and the dissolved alkaloid filtered into a flask and set aside. In a very short time both warts and prisms separated which turned out to be protopine. All fractions of this alkaloid were united and purified in the usual manner and finally recrystallized from a mixture of alcohol

and chloroform. The rather large prisms of protopine melted at  $204^{\circ}$ – $205^{\circ}$  (uncorr.).

To make doubly certain that this alkaloid was protopine one combustion was made:

0.4203 gram alkaloid gave 0.0467 gram carbon dioxide, and 0.196 gram water.

	Calculated for $C_{20}H_{19}NO_5$	Found.
Carbon.....	67.98	67.92
Hydrogen.....	5.38	5.23

It contains no methoxyl groups as determined by Zeissel's method. A periodide was obtained which crystallized in beautiful rosettes of a wine-red color. The formula was not determined because of lack of sufficient material.

#### ALKALOID IV.

This base is present in very small quantity and was obtained with great difficulty during the long course of fractional crystallization. It generally separated out along with chelidonine but the relative quantity was so small that complete separation consumed nearly as much time as the isolation of all the other alkaloids. The mixed fractions of chelidonine and this alkaloid were dissolved in acetic acid, diluted with water, placed in a separator, made alkaline with ammonia and shaken out with ether. After filtering into a flask, close watch was kept of the progress of crystallization and as soon as a small quantity of crystals had separated the ether was decanted into another flask, and just as carefully watched for the appearance of further crystals. This was repeated over and over again until about twenty-five small fractions were obtained that melted in the neighborhood of  $210^{\circ}$ . These were combined and the process of purification fairly begun when we lost about two-thirds of the product by an accident. Enough was saved, however, to observe some of its properties. The perfectly pure alkaloid melts at  $216^{\circ}$  (uncorr.). It crystallizes at times in extremely thin plates, and from their position on the side of the flask reminded us of the wings of butterflies. The most common form is shown in Fig. 6.

The acetic acid solution behaved with the usual alkaloidal reagents practically in the same manner as stylopine with the exception that the hydriodide formed by the addition of potassium iodide solution is amorphous instead of crystalline.

Color tests were made as follows:

A few drops of a solution of the free alkaloid were placed into each of the concave depressions of a white porcelain testing plate, and evaporated on the water-bath to dryness. In this way a very thin film of the alkaloid was distributed over the surface of the depression. A drop of the reagent was let fall into the cavity and brought in contact with the alkaloid.

Nitric acid.....slowly dirty yellow, then passing through violet, wine-red, dull green, and finally reddish-brown.  
Marquis' reagent.....first violet-blue then wine-red.  
Erdmann's reagent.....yellowish green to bright green.  
Froehde's reagent.....deep green, olive-green bordered with blue, finally all becoming blue.

Since this alkaloid seems not to have been found before, we have named it diphylline.

#### ALKALOID V.

In acid solutions this alkaloid is bright red in color, but is precipitated pure white with alkalis. The free alkaloid is extremely soluble in ether, more so than any of the others, which accounts for the fact that it is the last to crystallize out. The bluish fluorescent ethereal liquid, from which the four alkaloids mentioned had been eliminated because of their insolubility in ether, was treated with dry hydrochloric acid gas in a wash-bottle for an hour. The bright red salt collected on the exit tube, and on the bottom and side of the bottle. The ether was decanted and the red salt dissolved in hot water, cooled to just short of the crystallizing point, made alkaline with ammonia water and shaken out with ether. The filtered ethereal solution was set aside in a vacuum desiccator, over night. By morning almost white clusters of plates had separated that on exposure to air soon began to turn red. Not over 0.3 gram was obtained so that no analyses were attempted. This is without question the alkaloid which Schmidt and his pupils have named sanguinarine. From historical as well as etymological reasons it should be called chelerythrine, but we shall not add to the existing confusion by applying the names differently.

*Organic Acids.*—The organic acids which were in combination with the alkaloids in the original drug are now contained in the aqueous percolate of the marc in the form of ammonium salts. By the addition of strong alcohol most of the extraneous matter is removed in the form of a sticky mass. Convenient portions of

the percolate were treated in a 5 liter flask with successive portions of 96 per cent. alcohol until the precipitate which formed balled together into a gummy mass, upon vigorous shaking, leaving the supernatant liquid light colored and almost transparent. The latter was filtered into a 20 liter ice-jar and set aside in a cool place. After a few hours very light, fluffy, voluminous hemispherical masses of fine needles began to separate on the side of the jar. By adding more alcohol from time to time these masses grew enormously and the solution finally became practically exhausted of this crystalline substance. The liquid was siphoned off and the crystals removed with a spatula, and what at first appeared to be a large yield was compressed to small volume. These crystals were found to consist of a potassium compound extremely soluble in water, practically insoluble in alcohol. No odor of ammonia could be detected when a portion was boiled with strong potassium hydroxide.

Several methods for the purification of this compound were tried but the following was found to be the most satisfactory. Since this compound forms an insoluble lead salt the aqueous solution of the entire yield was precipitated with a solution of lead acetate. The white granular precipitate was collected on a filter and washed until the filtrate scarcely gave a test for lead. The lead salt was then suspended in water and decomposed with hydrogen sulphide. After warming slightly, the lead sulphide was removed by filtration and the filtrate which contained the free acid evaporated slightly to remove excess of hydrogen sulphide. To this solution precipitated calcium carbonate was added until there was no more effervescence, the whole being kept hot. The nearly colorless filtrate was set aside and at the end of several hours a magma of fine needles of the calcium salt had separated. By recrystallizing several times from hot water the salt was obtained nearly pure white. The latter was brought into aqueous solution again and treated with a slight excess of the silver nitrate solution, which threw down pure white needles of silver salt. This was collected on a filter, slightly washed, dissolved in hot water and then treated with an excess of hydrochloric acid. The filtrate upon cooling separated a mass of silky needles of the free acid. Several recrystallizations furnished a pure product. It is very sour and forms salts with a number of bases.

Since *Stylophorum diphylum* is so closely related to *Chelidonium majus*, botanically, we suspected that this acid is the same as the one found in the latter plant and named chelidonic acid by Probst. The characteristic yellow color of the potassium salt of chelihydronic acid, obtained when potassium hydroxide is added in excess to a solution of chelidonic acid, is also produced with our acid. A combustion was made of the desiccator-dried material, and the following results were obtained :

0.246 gram of the acid gave 0.3748 carbon dioxide and 0.0658 gram water.

	Calculated for $C_7H_4O_6.H_2O$ .	Found.
Carbon .....	41.58	41.55
Hydrogen.....	2.97	2.97

Since chelidonic acid has been so thoroughly investigated by Lerch<sup>1</sup> and others, we have contented ourselves with mere identification.

The alcoholic liquid that had been deprived of potassium chelidonate was distilled *in vacuo* for the recovery of the alcohol and the aqueous residue remaining concentrated to small volume. The inert matter was removed with alcohol as before. The filtrate was set aside and after many days fine needles separated and projected from the side of the jar. These were removed, purified and found to be the ammonium salt of chelidonic acid.

**Coloring-Matter.**—As was stated above the filtered alkaline aqueous liquids, from which the alkaloids had been washed by means of ether, were reserved for the purpose of isolating the coloring-matter. The greater part of the protopine (alkaloid III) was recovered from this solution. The liquid still retained its full depth of color and was shaken out with several liberal portions of acetone. The deeply colored acetone solution was filtered and the acetone removed by distillation. The dark, bitter residue was taken up with a small quantity of water and treated with a solution of lead acetate. The precipitate was collected and then boiled with water which took out considerable of the coloring-matter. From the filtrate after concentration there separated, after several days, small crystals of a yellowish-red color which, when dissolved in water, imparted to it the color of the original solution. From analogy we believe that this body is the same as Probst's chelidoxanthin but the quantity was too small for further study. Some interesting questions have presented themselves in connec-

<sup>1</sup> *Monatsh. Chem.*, 29, 131.

tion with this substance which we hope to be able to answer in the near future.

#### SUMMARY.

*Stylophorum diphylllum* contains at least five alkaloids as follows:

Chelidonine	$C_{20}H_{19}NO_3 \cdot H_2O$	melting-point	136° (uncorr.).
Stylopine	$C_{19}H_{19}NO_3$	"	202° "
Protopine	$C_{20}H_{19}NO_3$	"	204°-205° "
Diphylline		"	216° "
Sanguinarine			
Chelidonic acid	$C_7H_4O_6 + H_2O$		
Chelidoxanthin (?)			

The study of this plant and its constituents will be prosecuted during the coming year, Professor Lloyd having again arranged for the collection of a large quantity of authentic material. We take pleasure in extending to Professor Lloyd our sincere thanks for this assistance without which the investigation would not have been possible.

We also take this opportunity of expressing our appreciation of the generosity of Messrs. F. Stearns & Co., for furnishing the funds necessary for the promotion of the work.

SCHOOL OF PHARMACY, UNIVERSITY OF  
MICHIGAN, ANN ARBOR, MICH.

### THE DISCOVERY OF NITROGLYCERINE IN AN EXHUMED BODY.

By G. G. POND.

Received October 1, 1901.

THE writer has not been able to find any record of the detection of nitroglycerine in a dead body, in cases of suspected poisoning, though this substance is included in the accepted complete schemes for toxicological examination of human organs.

On the fourteenth of March, 1901, the stomach, liver, kidneys, and spleen of a woman of twenty-two years were brought to this laboratory for examination, direct from an autopsy which had been made on that date. This woman had died on the tenth of January previous, in convulsions supposed to have been brought about by the use of instruments, or by drugs or medicines administered with intent to produce abortion. The woman had been ill for only twenty-four hours, and during this time nothing had been administered by the attending physicians through the mouth; small doses of morphia had been given hypodermically.



The body had been thoroughly "embalmed" with an arsenical formaldehyde fluid which contained some glycerine, mere traces of mercury, and a little oil of citronella, otherwise nothing of significance. The embalming fluid gave no reaction whatever for nitric or nitrous acid under the most careful tests. The embalmed body was buried January 14th; thus two months elapsed before the disinterment on the fourteenth of March. When received at the laboratory the organs were all in a state of excellent preservation. The stomach contained no appreciable contents distinguishable from the embalming fluid. A preliminary examination for volatile substances was conducted upon 91 grams of that organ, about one-fourth of the entire weight of the stomach and fluid. This examination was carried out according to Dragendorff.<sup>1</sup> The material was comminuted, acidified with pure tartaric acid, and after the addition of 50 cc. of water, was distilled with steam. Some 100 to 125 cc. of the distillate were secured which possessed a peculiar odor resembling formaldehyde but quite modified, somewhat like the lower fatty acids. It exhibited an acid reaction, and contained in suspension minute oily globules. This distillate gave no precipitate with silver nitrate, with or without nitric acid, gave reaction with Schiff's reagent (fuchsine bleached with sulphurous acid) for aldehyde, also all other aldehyde reactions. It gave no reaction for hydrocyanic acid, for chloroform, phenols, benzaldehyde, halogens, sulphur or alcohol.

The steam distillate was extracted with ether, the ether evaporated and a small residue secured possessing nearly the consistency of vaseline, slightly opalescent, and nearly colorless. This residue was free from halogens and sulphur, gave nitric acid reaction with sulphuric acid and brucine, also with sulphuric acid and diphenylamine. It had a decided taste, sweetish, spicy and slightly burning, and was explosive. Repeatedly dissolved in ether and evaporated as before, it exhibited the same properties. It exploded violently when heated on a platinum spoon or otherwise, also when struck on an anvil, etc.

Some eight or ten explosions were secured with it at the date of the analysis; three or four more at the time of the trial in April, and the last remnants exploded distinctly as late as August 21st.

The total weight, after we felt the identification as nitroglycerine to be complete, was 9.5 mg., or calculated for the whole

<sup>1</sup> Georg Dragendorff: "Ermittlung von Giften," vierte Auflage, 1895, p. 84, *et seq.*

stomach, 0.7 grain, equivalent approximately to from 1 to 1½ teaspoonfuls of the officinal 1 per cent. solution.

A comparative quantity of pure nitroglycerine, acidified with tartaric acid, distilled with steam in a similar apparatus, at the same rate, yielded a distillate in which oily drops were observable, and its ethereal extract when evaporated yielded a residue which exploded with the same readiness. A similar examination of other parts in our possession did not reveal any nitroglycerine, and none of the intestines had been taken at the autopsy.

The defendant was convicted of the use of instruments, and the presence of nitroglycerine was not accounted for by the testimony. It was a theory of the prosecuting attorneys, however, that nitroglycerine had been administered, in ignorance, as a heart stimulant.

I am indebted to Dr. F. E. Tuttle and to Dr. F. J. Pond, for their assistance in this work.

CHEMICAL LABORATORY OF THE PENNSYLVANIA  
STATE COLLEGE, August 21, 1901.

[CONTRIBUTIONS FROM THE HAVEMEYER LABORATORIES OF COLUMBIA  
UNIVERSITY, No. 57.]

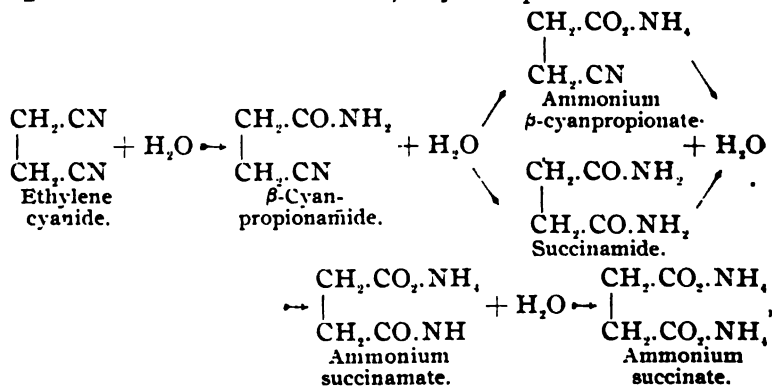
## ON THE PRODUCTION OF THE IMIDES OF SUCCINIC AND GLUTARIC ACIDS BY THE PARTIAL HYDRATION OF THE CORRESPONDING NITRILES.<sup>1</sup>

BY MARSTON TAYLOR BOGERT AND DAVID C. ECCLES.

Received November 5, 1901.

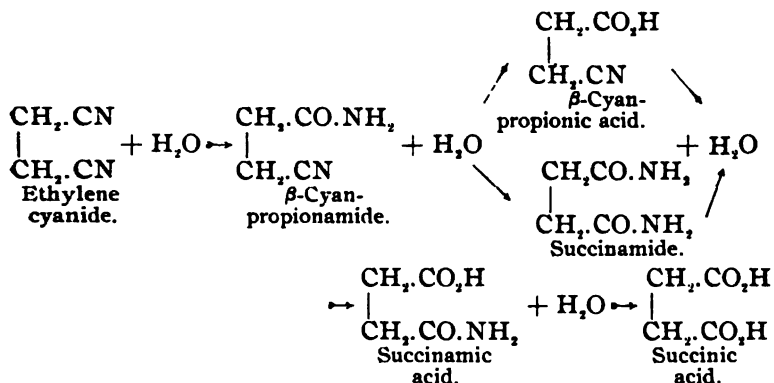
### THEORETICAL.

THE hydration of ethylene cyanide, by the addition of successive molecules of water, may be represented as follows:



<sup>1</sup> Read before the New York Section of the American Chemical Society, Nov. 1, 1901.

or, if this hydration be carried out in the presence of a strong mineral acid, the products will be as follows :



For the conversion of the nitrile to the acid, therefore, at least four molecules of water are necessary, and the question naturally arises as to what will occur when less than this amount of water is present, say two molecules of water in sealed tubes, and with one equivalent of a mineral acid to set free the cyanpropionic acid from its ammonium salt.

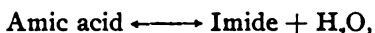
Of course, it was hardly to be expected, in our experiments to answer this question, that the hydration would proceed quantitatively and exclusively along one line, yielding, for example, only amide or cyan acid, but that in all probability any or all of the various hydration products would have to be reckoned with. Under conditions of heat and pressure, however, the addition of exactly two molecules of water to one molecule of the nitrile, and in presence of exactly one equivalent of a strong mineral acid, should yield one and the same major product, no matter what the course of the hydration. That product is the imide.

$\beta$ -Cyanpropionic acid rearranges to the imide, succinamide loses ammonia with formation of the imide, succinamic acid gives the same body by loss of water, and it has been shown in this laboratory<sup>1</sup> that when succinic acid and its nitrile are heated together in sealed tubes succinimide is the product.

To be sure, these changes to the imide occur at quite different temperatures, the production of the imide from succinic acid and its nitrile, or from succinamide, requiring a temperature of 200°

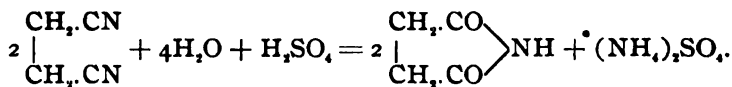
<sup>1</sup> Miller: *This Journal*, 16, 443 (1894); Seldner: *Am. Chem. J.*, 17, 532 (1895); Mathews: *This Journal*, 20, 654 (1898).

or over, while succinamic acid probably loses its water at a much lower point, and  $\beta$ -cyanpropionic acid rearranges to the imide at still lower temperatures. It was hoped, consequently, that the temperature at which the reaction took place, and the nature of the by-products separated, might indicate whether the course of the hydration proceeded through the cyanpropionic acid or the amide. The problem is somewhat complicated by the fact that, while only two molecules of water might be added, succinamic acid, although theoretically requiring three molecules for its quantitative production, might be continuously formed in small amount and immediately break up again into imide and water, the net amount of water, therefore, used up in the reaction being but two molecules; the production of the imide might thus occur at low temperatures and still the course of the hydration be through the amide. Then, again, the formation of imide from amic acid is partly reversible:



and succinamic acid and most of its salts change quite easily, in presence of water, to succinic.

The following reaction was taken as the basis of our laboratory work:



As the ratio of sulphuric acid to water in such a reaction is entirely independent of the particular nitrile to be hydrated, a standard acid was prepared containing sulphuric acid and water in exactly this proportion, and then the required amount measured out volumetrically. In most cases, 5 grams of the nitrile were used at a time, and the reaction carried out in sealed tubes at temperatures varying from  $100^\circ$ – $200^\circ$ .

As expected, the imide was the chief product in all cases. Cyanpropionic acid, cyanpropionamide, and succinic acid were not found in any of the tubes. The absence of  $\beta$ -cyanpropionic acid and its amide is not strange, as the hydration would certainly carry the cyanpropionamide further, and cyanpropionic acid would rearrange to succinimide at the temperature of the reaction. That no succinic acid was found, however, seems to argue that the major part of the imide did not come from continuous formation and breaking down of the amic acid, for the

amic acid is so easily hydrated to succinic that in the early stages of the reaction, when small amounts of the amic acid had formed and there was still an excess of uncombined dilute sulphuric acid present, it seems difficult to understand why no trace of succinic acid resulted. Any succinic acid produced in the reaction should have been recovered unchanged, as the temperature was in no case high enough or maintained for a sufficient length of time to cause the acid to combine with the unchanged nitrile and thereby yield the imide.

If the imide did not owe its origin to amic acid, it could not have come from the amide at all, as the temperature was too low to drive ammonia out of the amide. The only remaining explanation is that the chief source of the imide was the rearrangement of the cyanpropionic acid, and that the hydration, therefore, proceeded mainly along this line. Small amounts of succinamide and of succinamic acid were, however, isolated from many of the tubes, the presence of the latter being quite possibly due to a partial rehydration of the imide, to establish the equilibrium between the system-imide, amic acid, water. The production of imide in tubes 5 and 6, where no mineral acid was present, also seems more likely to be due to a decomposition of ammonium cyanpropionate than of ammonium succinamate. That the hydration should tend to complete itself upon one cyanogen group before attacking the next is quite analogous to the action of oxidizing agents, halogens, etc., upon similar straight chain compounds.

As the question of temperature determines the relative yield of imide, it may be said, briefly, that, for the production of succinimide, it is best to heat for about two days at  $165^{\circ}$ – $175^{\circ}$ . Below this point the hydration is slow and incomplete; above it, partial carbonization follows. For glutarimide, a temperature of  $180^{\circ}$ – $200^{\circ}$  is desirable.

#### EXPERIMENTAL PART.

*For Succinimide.*—Sealed tubes were prepared containing 5 grams of ethylene cyanide, and a mixture of two molecules of water to half a molecule of absolute sulphuric acid (= 3.6 cc. of a sulphuric acid of 1.478 specific gravity). These tubes were heated at various temperatures and for varying lengths of time, the product being a brown crystalline solid usually more or less moist according to the temperature of the reaction and the dura-

tion of the heating. The method of working up the contents of the tubes was based upon the following considerations:

The bodies possibly present in the tubes after heating are the various hydration products already indicated, succinimide, ammonium sulphate, excess of sulphuric acid and water. By rubbing up such a mixture with a thin paste of barium carbonate, the excess of sulphuric acid and most of the ammonium sulphate form barium sulphate; cyanpropionic acid, succinamic and succinic acids, yield barium salts; ethylene cyanide, cyanpropionamide, succinamide and succinimide remain unchanged. If the mass be then evaporated, carefully dried, powdered, and extracted with absolute alcohol, ethylene cyanide, cyanpropionamide, and succinimide will be dissolved out, while succinamide remains for the most part insoluble. Ethylene cyanide, cyanpropionamide, and succinimide can then be separated by selection of suitable solvents, etc. The residue insoluble in absolute alcohol may contain succinamide, the barium salts of cyanpropionic, succinamic and succinic acids, barium carbonate and sulphate, ammonium carbonate, and, possibly, a little unchanged ammonium sulphate. By extraction with water, all except barium carbonate and sulphate are dissolved, and ignition of the residue will show no organic matter. Addition of sulphuric acid to the aqueous solution will then liberate the organic acids from their barium salts, when they can be removed by repeated extraction with ether. Finally, if barium carbonate be added to the acid solution after the ether extraction, and the filtrate from precipitated barium sulphate evaporated and the residue ignited, the carbonizing of the residue will show the presence of amide or of acids insoluble in ether, which may then be extracted by proper solvents until the ignition of the residue shows no organic matter.

As examples, the following tubes may be mentioned: Tubes 1, 2, 3, and 4 all contained 5 grams of ethylene cyanide, two molecules of water, and half a molecule of sulphuric acid. They were heated as follows:

No. 1, six hours at  $131^{\circ}$  to  $138^{\circ}$ .

No. 2, six hours at  $142^{\circ}$  to  $155^{\circ}$ , and then three hours at  $158^{\circ}$  to  $165^{\circ}$ .

No. 3, six hours at  $154^{\circ}$  to  $162^{\circ}$ .

No. 4, five hours at  $160^{\circ}$  to  $170^{\circ}$ , and then six and a half hours at  $159^{\circ}$  to  $165^{\circ}$ .

The contents of the tubes were worked up as already outlined. Succinimide was found in all of the tubes, the amount increasing with the rise in temperature and the duration of the heating. No. 1 contained much unchanged cyanide. Small amounts of amic acid occurred in all of these tubes, and traces of what appeared to be amide were separated in several.

No. 5 contained 5 grams of ethylene cyanide, two molecules of water, and no sulphuric or other mineral acid. It was heated for five hours at  $153^{\circ}$  to  $173^{\circ}$ . The mixture in the tube then appeared as a brownish liquid containing oily globules, and with a strong odor of ammonia. Most of the cyanide appeared unchanged, as scarcely any imide could be detected.

No. 6 carried 5 grams of the cyanide, one molecule of water, and no mineral acid. It was heated for six hours at  $153^{\circ}$  to  $173^{\circ}$ . The tube contents were then brown and semisolid. Succinimide in large amount was separated, a small amount of amic acid, traces of succinamide, but no cyanpropionamide was discovered.

*For Glutarimide.*—Trimethylene cyanide was heated in sealed tubes with two molecules of water and half a molecule of sulphuric acid, for five to ten hours at  $155^{\circ}$  to  $200^{\circ}$ , and the products of the reaction separated in essentially the same manner as for the succinimide tubes. Glutarimide was isolated in large amount (60 per cent. of theory), but no amide or amic acid could be detected, except the imide, the tubes containing only unhydrated cyanide. A temperature of  $180^{\circ}$  to  $200^{\circ}$  is necessary for the success of the hydration.

ORGANIC LABORATORY, HAVEMEYER HALL,  
COLUMBIA UNIVERSITY,  
July 1, 1901.

## ON THE DETERMINATION OF CITRATE-INSOLUBLE PHOSPHORIC ACID.

BY C. D. HARRIS.

Received October 12, 1901.

THE method used in the laboratory of the North Carolina Department of Agriculture up to recently was as follows:

Two grams of the sample to be analyzed were washed free of water-soluble phosphoric acid. Then 100 cc. of strictly neutral ammonium citrate solution (sp. gr. 1.09) in an 8-ounce Erlenmeyer flask, was heated to  $65^{\circ}$ , in a water-bath, keeping the

flask loosely stoppered to prevent evaporation. When the citrate solution in the flask had reached  $65^{\circ}$ , the filter containing the washed residue from the water-soluble phosphoric acid determination was dropped in and the flask stoppered tightly and shaken until the filter-paper was reduced to a pulp. The flask was then placed back, loosely stoppered, in the water-bath, the temperature of which was so maintained as to give exactly  $65^{\circ}$  in the citrate flask. The flask was shaken every five minutes. At exactly thirty minutes from the time the filter and the residue were introduced, the flask was removed from the bath and the contents filtered as rapidly as possible. The residue on the filter was then washed thoroughly with distilled water at  $65^{\circ}$ . The filter and its contents were then returned to the original digestion flask, and 40 cc. nitric acid and 20 cc. hydrochloric acid were added and boiled down to about 15 or 20 cc. concentration.

The solution was diluted to 200 cc., and 40 cc., corresponding to 0.4 gram of fertilizer, were measured into a 500 cc. Erlenmeyer flask. Add 10 or 12 grams ammonium nitrate and a little distilled water. The excess of acid is neutralized with ammonia. When the contents had cooled 30 cc. of recently filtered molybdic solution were added and the flask, after securely stoppering with an ordinary rubber stopper, was placed in a Wagner shaking machine which was revolved by a hot-air motor and shaken for thirty minutes. The shaking machine was maintained at from 45 to 55 revolutions per minute, as this velocity has been found to give the maximum agitating efficiency. The flask was removed from the shaking machine and contents filtered, washed, returned to the shaking flask, and titrated.

The method of filtering the contents of the flask, after heating with citrate solution, through a funnel in which was a very thick filter-paper and platinum cone and using pressure for rapid work, was found to be unsatisfactory in three ways:

*First.*—The filter-paper was likely to burst and thereby necessitate another filtration.

*Second.*—It was very difficult to fit the filter-paper in the funnel so that no air would get in around the sides and retard the filtration.

*Third.*—It was entirely too slow for rapid work.

Having encountered these difficulties, the Hirsch funnel was



tried, using a closely fitting filter-paper in the bottom, but it was found very difficult to fit this filter-paper so that none of the substance would pass down around the edges and render the determination valueless.

This method not proving satisfactory, the Hirsch funnel, using filter-paper pulp in the bottom, was next tried. It was found that in order not to allow any of the substance to pass through, it was necessary to use a large amount of pulp and this rendered the filtration as slow as in the first case.

This method being abandoned, a filter of the following construction was tried: Take a carbon filter, and place in the bottom of it a tightly fitting perforated porcelain disk, to which is attached a small wire that extends down beyond the small end of the carbon filter. A rubber stopper is then fitted tightly in a pressure bottle and the carbon filter passed through it. A layer of asbestos is placed on the disk in the carbon filter and by the aid of pressure this gave entire satisfaction.

By this method it took only from thirty to forty minutes to filter and wash the residue, while with the old way it took from one and a half to two hours.

Where a large number of samples are to be analyzed one will not only save a great deal of time but the residue can be washed more thoroughly.

Some difficulty was also experienced from the cracking of the ordinary rubber stopper used in the shaking flask, when revolving in the shaking machine, because the solution would leak out around the crack in the rubber stopper. To prevent this, antimony rubber stoppers were tried and these proved very successful as no leaking has been noticed since they were put in.

In another part of the method, rapidity will also be increased by proceeding as follows: Just before adding the molybdic solution, to precipitate the phosphoric acid, neutralize the excess of acid with ammonia, and then add 10 or 12 grams of ammonium nitrate; then the molybdic solution can be added immediately, for the ammonium nitrate cools the solution down to where it is safe to precipitate and no waiting to cool is necessary as is the case if ammonium nitrate is added before the excess of acid is neutralized.

## A HYDROLYTIC DERIVATIVE OF THE GLOBULIN EDESTIN AND ITS RELATION TO WEYL'S ALBUMINATE AND THE HISTON GROUP.

BY THOMAS B. OSBORNE.

Received September 28, 1901.

It is well known that globulins, after precipitation from salt solutions, either by dilution or dialysis, usually do not redissolve completely in solutions of a neutral salt.

Weyl<sup>1</sup> states that, on long contact with water, globulins gradually become insoluble in neutral sodium chloride solutions of every concentration, and designates the substance thus formed as "albuminate." Very recently Starke<sup>2</sup> calls attention to the action of water on globulin and states that the precipitated globulin, when washed but a few times with water, always becomes nearly, or quite, insoluble in saline solutions, whereas globulin, which is precipitated by saturating its solution with neutral salts, can be kept for months in the saturated brine without losing its solubility.

In the presence of a very little acid this change from a soluble to an insoluble state appears to take place more rapidly. Thus a globulin thrown down by carbonic acid from a salt solution very soon becomes, to a large extent, insoluble in neutral solutions of sodium chloride. Myosin is rapidly changed into an insoluble form by the acid which develops in the muscle substance after death, and legumin extracted from leguminous seeds is soon converted into a form insoluble in salt solutions, unless the acid is neutralized as soon as the extract is made.

The following investigation makes it probable that the insoluble product, in the case of edestin at least, results from the hydrolytic action of hydrogen ions, and that this change in the protein molecule is the first of a series which leads to the formation of "acid albumin."

In the case of edestin and other proteins of the endosperm, this change from a soluble to an insoluble form takes place much less readily than in proteins from physiologically active animal tissues. It is also true that the proteins of the wheat *embryo*, which is likewise capable of great physiological activity, are also much

<sup>1</sup> *Ztschr. physiol. Chem.*, 1, 72 (1877.)

<sup>2</sup> Starke: *Ztschr. Biol. n. f.*, 22, 425.

more prone to become insoluble, in the way described, than those of the *endosperm* of wheat and other seeds.<sup>1</sup>

Since this derivative of edestin is a definite substance, well characterized by its properties and reactions, I propose to call it *edestan*, and if, as seems probable, the other protein bodies yield similar derivatives, these may be named in a like manner by changing the termination *in*, usually applied to the protein substance, to *an*. The group of substances belonging to this class may be called proteans, thus following the practice whereby the more altered and basic hydrolytic protein derivatives are designated proteoses, and the individual members albumose, caseose, etc.

It is important that a distinction should be made between these proteans and those products which result from a more profound change in the protein molecule, caused by the action of stronger acids and alkalis, and which are now known as acid and alkali albumin.

#### A. ACTION OF WATER ON EDESTIN.

Pure water, because it is but slightly ionized, has little effect on pure edestin<sup>2</sup> at the room temperature. If, however, carbonic acid is present, edestan is formed in decidedly larger amount.

Gram portions of pure and perfectly neutral edestin were suspended in water, agitated frequently and exposed to different temperatures for definite periods of time. An equal volume of 20 per cent. sodium chloride solution was then added to each, and the solution made neutral to phenolphthalein, by which the unaltered edestin was at once dissolved and the formation of edestan was stopped. The edestan was allowed to settle over night and was then easily collected on a filter and thoroughly washed with 10 per cent. sodium chloride brine, until the washings showed no trace of the xanthoproteic reaction.

Nitrogen was determined in the residue and the amount of edestin calculated by multiplying the nitrogen by 5.4, since, as will be shown later, edestan contains 18.5 per cent. of nitrogen. The results obtained were the following:

<sup>1</sup> Cf. Martin: *Jour. Physiology*, 8, viii, (1887).

<sup>2</sup> For the properties of edestin, and its relations to acids and alkalis, the paper following this should be consulted, in which will be found in detail the evidence on which are based many of the statements made in this paper, concerning edestin and its compounds. Also, Osborne, "On Some Definite Compounds of Protein Bodies," *This Journal*, 21, 486.

TABLE I.—PERCENTAGE OF EDESTAN FORMED BY CONTACT WITH WATER.

Treated with sodium chloride solution after 6 hours.				
10 per cent. NaCl at 20°.	Water +CO <sub>2</sub> at 20°.	Pure water at 20°.	Pure water at 30°.	Pure water at 50°.
2.16	6.75	4.32	7.11	29.00

The portion which was treated with sodium chloride solution stood exactly as long as the others before filtration. The insoluble matter which this contained consisted of a little edestan which was originally present in the preparation and of edestan which was formed by treatment of the edestin with the salt solution. The above figures show that even at 20° a notable quantity of edestan is formed by water alone and that the quantity is decidedly greater if the water contains carbonic acid. At 50° about four times as much edestan was formed as at 30°, and nearly eight times as much as at 20°, which agrees with the fact that the velocity of such a reaction is about doubled by each increase of 10° in the temperature.

## B. ACTION OF ACIDS ON EDESTIN.

Edestin combines with small, but definite, quantities of acid to form salts in which the edestin molecule is unchanged. In the presence of an excess of acid, above that required to form these salts, edestin is converted by the free hydrogen ions into edestan, as the following experiments show.

Gram portions of pure, neutral edestin were suspended in water enough to make a final volume of 20 cc., and to the different portions the quantity of centinormal acid stated in the following table was added. After being frequently agitated during the times indicated, the acid was neutralized by an equivalent quantity of decinormal potassium hydroxide solution and the amount of edestan that had formed was determined, as in the preceding experiments with water.

TABLE II.—PERCENTAGE OF EDESTAN FORMED BY ACIDS AT 20°.

9 cc. HCl 100	14 cc. HCl 100	18 cc. HNO <sub>3</sub> 100	19 cc. HNO <sub>3</sub> 100	20 cc. HNO <sub>3</sub> 100
3 hours. 20 hours.	3 hours. 20 hours.	24 hours. 24 hours.	24 hours. 24 hours.	24 hours. 24 hours.
9.01 12.15	29.80 33.55	68.38	75.20	79.02

These figures, compared with those of Table I, show that edestin yielded much more edestan in contact with acids than in contact with water, and also that the percentage of edestan produced increased with the amount of acid.

One gram of this air-dry edestin preparation (equivalent to

0.9300 gram of water-free edestin) can combine with 13 cc. of centinormal hydrochloric acid, so that in the portion containing 9 cc. only that amount of acid was free which was produced by the hydrolytic dissociation of the compound formed, whereas the portion with 14 cc. of acid contained, in addition, a small amount of free acid, the effect of which is shown by the greater amount of edestan formed in it. That, in both cases, only a little more edestan was formed during twenty hours than during three hours is explained by the fact that edestan unites with a larger proportion of acid than does edestin, and consequently, as the proportion of edestan increases the proportion of free acid diminishes. With 20 cc. of nitric acid 79 per cent. of the edestin was converted into edestan.

From the salts of edestin, such as usually constitute the crystalline preparations as heretofore made by the usual methods, edestan may be prepared just as from the pure and neutral edestin which was used in the preceding experiments. One gram of a preparation consisting of edestin mono- and bichloride, chiefly the latter, and which already contained 6.32 per cent. of edestan, that had been formed during its preparation, was suspended in water and brought into solution by adding 3 cc. of centinormal hydrochloric acid. The added acid, as well as that originally combined with the edestin,<sup>1</sup> was at once neutralized, an equal volume of 20 per cent. sodium chloride solution added, which dissolved the unaltered edestin, and the edestan was determined as described above. Deducting the edestan originally present in the preparation, it appeared that during the very brief action of the acid, 3.49 per cent. of edestan had been formed. In a similar experiment with 3 cc. of acid, which was left in contact with the preparation for twenty hours before neutralization, 29.5 per cent. of edestan was formed. Using 10 cc. of acid, instead of 3 cc., 13.32 per cent. of edestan was formed at once, and 70.46 per cent. after twenty hours' contact.

That the amount of edestan formed in a given time depends on the degree of ionization of the acid was shown by suspending gram portions of neutral edestin in 6 cc. of water, adding 14 cc. of centinormal hydrochloric, phosphoric and acetic acids, respectively, and, after frequently agitating for about two hours at 20°, determining the amount of edestan formed in each.

<sup>1</sup> One gram of this preparation contained acid equivalent to 11 cc. of  $\frac{\text{HCl}}{100}$ .

TABLE III.—PERCENTAGE OF EDESTAN FORMED BY EQUIVALENT QUANTITIES OF DIFFERENT ACIDS UNDER THE SAME CONDITIONS.

HCl.	H <sub>3</sub> PO <sub>4</sub> .	H <sub>4</sub> C <sub>2</sub> O <sub>6</sub> .
19.29	16.02	5.65

The solution of phosphoric acid used in this experiment contained 0.98 gram of H<sub>3</sub>PO<sub>4</sub> per liter, being made on the assumption that this acid behaves towards edestin as a monobasic acid. The much smaller quantity of edestan formed by acetic acid, compared with that formed by hydrochloric acid, is in accord with the lesser ionization of this acid.

#### C. COMPOSITION OF EDESTAN.

Ten grams of a preparation of crystallized edestin chloride were suspended in water, in a glass-stoppered bottle and 30 cc. of decinormal hydrochloric acid were gradually added. After the resulting clear solution had stood at the room temperature for about two hours, it was made neutral to phenolphthalein by adding 38 cc. of decinormal potassium hydroxide solution, the 8 cc. in the excess of the 30 cc. of added acid being required to neutralize the acid originally combined with the edestin preparation.

The curdy precipitate that formed on neutralizing, was washed thoroughly with 10 per cent. sodium chloride solution and then with water, until chlorides were removed, and finally with absolute alcohol. Dried over sulphuric acid, this formed preparation 1, which weighed 6.82 grams.

This experiment was repeated with another preparation of edestin chloride, the acid solution allowed to stand over night at a temperature below 10°, and then 50 cc. of decinormal potassium hydroxide solution were added. Although this excess of alkali was more than sufficient to dissolve the entire quantity of substance which was precipitated by neutralization, had this been unchanged edestin, nevertheless very little protein matter was dissolved by it. The precipitate was filtered out, washed with water, dehydrated with absolute alcohol and found to weigh 8 grams after drying over sulphuric acid. This formed preparation 2.

Preparations of edestin chlorides, which contain the water-soluble bichloride, yield aqueous solutions, from which the protein matter is precipitated by a little sodium chloride. The precipitate thus formed is never wholly soluble again in stronger solutions of sodium chloride, a part being converted into the

so-called "albuminate" of Weyl. In order to establish the relations of this substance with that produced by the action of acids on edestin, under known conditions, a quantity of edestin, that had been obtained as a crystalline precipitate by cooling a warm dilute sodium chloride extract of hemp-seed meal, was washed by decantation with water until the sodium chloride was largely removed, whereupon the edestin began to dissolve.

When most had passed into solution, enough sodium chloride, in substance, was added to the clear aqueous solution containing the edestin to form an 8 per cent. brine. The edestin, at first precipitated by partial solution of the salt, mostly redissolved in the stronger brine that formed when all the salt had gone into solution.

The part that did not dissolve was filtered out and washed thoroughly with salt solution until all the globulin had been removed and then extensively with water. As the salt was washed away, the residue became gelatinous and dissolved slightly, so that it could no longer be washed on a filter. It was therefore suspended in water and made exactly neutral to phenolphthalein with very dilute potassium hydroxide solution. This converted it into a curdy precipitate which was easily filtered out and washed. In this condition it resembled, in all respects, the edestan obtained by neutralizing the hydrochloric acid solutions just described. After washing thoroughly with water and dehydrating with absolute alcohol, this preparation, 3, was dried at  $110^{\circ}$  and analyzed with the results given below. Preparations 1 and 2 were likewise dried at  $110^{\circ}$  and analyzed.

TABLE IV.—COMPOSITION OF EDESTAN.

	1	2	3	Edestin.
Carbon .....	51.48	51.91	51.69	51.50
Hydrogen .....	6.91	6.96	6.98	7.04
Nitrogen .....	18.51	18.49	18.49	18.69
Sulphur .....	1.00	0.99	0.92	0.88
Oxygen .....	22.10	21.65	21.92	21.89
	100.00	100.00	100.00	100.00
Ash .....	0.55	0.06	0.14	

Between these analyses and that of edestin no sufficient difference exists to enable us to detect any change in ultimate composition caused by its conversion into edestan. A strict comparison of the reactions of 1 and 2 with those of 3 showed that these were one and the same substance.

## D. REACTIONS OF EDESTAN.

Edestan prepared as just described is a voluminous, dusty, white powder which swells somewhat in water and forms a colorless, transparent jelly with very dilute hydrochloric acid. Whether a true solution was formed by the dry powder in this extremely dilute acid could not be ascertained since the opalescent fluid that resulted could not be filtered clear.

Dry, neutral edestan is scarcely soluble, even in strong ammonia, but the gelatinous mass, formed by treating the substance with very dilute hydrochloric acid, is slightly more soluble, though in either case the amount dissolved by ammonia is very small. The solution in ammonia yields a precipitate with ammonium chloride; consequently when hydrochloric acid is added to the ammoniacal solution a precipitate forms, even when much of the ammonia is unneutralized. The ammoniacal solution is not precipitated by sodium chloride.

A strong solution of edestan, which, however, probably contains a little unaltered edestin, may be prepared by dissolving edestin in centinormal hydrochloric acid in the proportion of 30 cc. to each gram and allowing the solution to stand for at least twenty-four hours. One-third of the acid may then be neutralized by adding the requisite quantity of very dilute potassium hydroxide solution. An opalescent, unstable, supersaturated solution results, which can be filtered nearly clear and, if abundantly diluted, yields no precipitate within several hours. Such a solution of edestan chloride yields a precipitate with 10 per cent. ammonia, which is soluble in a considerable excess, the resulting solution being readily precipitated by ammonium chloride. By decinormal ammonia solution the substance is precipitated but not redissolved, even by a very large excess of this ammonia solution.

The aqueous solution of edestan chloride yields a precipitate with a very little ammonium or sodium chloride, the latter being readily, the former with difficulty, dissolved by an excess of ammonia.

With nitric acid, edestan gives a precipitate completely soluble on warming but reprecipitated on cooling.

With potassium phosphotungstate, sodium phosphomolybdate or sodium picrate, edestan chloride forms slimy precipitates. With



a solution of ovalbumin, edestan chloride yields an abundant precipitate.

Mercuric chloride forms no precipitate in a dilute solution of edestan chloride, nor in a relatively strong one, unless a considerable amount of this reagent is added.

Very dilute hydrochloric acid does not precipitate edestan, but the strong acid gives a precipitate, which dissolves in a sufficient excess of concentrated acid.

#### E. THE AMOUNT OF ACID WITH WHICH EDESTAN COMBINES.

Edestan exists in preparations of edestin chlorides in combination with acid. The amount of acid with which this substance forms a compound, sparingly soluble in water, appears to be definite, as the following experiments show.

A quantity of a preparation of edestin chloride was dissolved, as far as possible, in 10 per cent. salt solution and the insoluble edestan was allowed to settle. This was first washed thoroughly with salt solution, until the edestin was removed, and then with water, in which a very little dissolved, while the remainder formed a gelatinous mass. The latter was suspended in water and dialyzed until the sodium chloride was removed. The dialyzer then contained an opalescent fluid and a voluminous precipitate. Of this fluid, 25 cc. were made neutral to phenolphthalein by adding 2.5 cc. of a centinormal solution of potassium hydroxide and by evaporating and drying the residue at  $110^{\circ}$  was found to contain 0.1165 gram of substance. The same volume drawn from the bottom of the dialyzer, which contained much of the undissolved matter, was made neutral by 11 cc. of the alkali and contained 0.4710 gram of substance. These quantities correspond to an acidity of 21.5 and 23.4 cc., respectively, of a centinormal solution per gram of edestan. A repetition of this experiment gave essentially the same result.

A quantity of the insoluble matter which remained on treating another preparation of edestin chloride with 10 per cent. sodium chloride brine was thoroughly washed with salt solution, once with water and finally with dilute alcohol, until all the salt was removed. A quantity of the still moist substance was then suspended in water, finely divided by straining through fine bolting-cloth, and 4 cc. of decinormal potassium hydroxide solution added, which was decidedly in excess of the quantity

necessary to make the mixture neutral to phenolphthalein. After agitating continuously for some time, the excess of alkali was neutralized by 2.1 cc. of decinormal hydrochloric acid, which showed that 1.9 cc. of the alkali had been neutralized by the acid combined with the substance. By evaporating and drying the residue at  $110^{\circ}$  it was found that 0.9430 gram of edestan was present in the mixture, from which it appears that its original acidity was equal to 20.1 cc. of a centinormal solution per gram.

Another portion of this substance was suspended in water in a finely divided state and brought into solution by adding 2 cc. of decinormal hydrochloric acid and shaking for some time. The solution was then made neutral to phenolphthalein, by adding 3 cc. of decinormal potassium hydroxide solution, and the amount of dissolved edestan found to be 0.5039 gram, from which it is seen that its original acidity was equal to 20 cc. of a centinormal solution per gram.

This quantity is just three times the acidity of edestin monochloride and one and a half times that of the bichloride; consequently if edestan is formed from edestin without any notable change in molecular weight, this substance occurs in preparations of edestin chlorides as a trichloride, assuming edestin to have a molecular weight of about 14,500.

Bang<sup>1</sup> has recently reviewed the reactions of the histons and concludes that for the present these may be defined as follows: In neutral solution the histons are precipitated by the cautious addition of ammonia, the precipitate in the presence of an ammonium salt very soon becoming insoluble in an excess of ammonia. They give a precipitate with nitric acid, which dissolves on heating and reappears on cooling. They are precipitated from neutral solution by heating, if their solutions contain some sodium chloride, not, however, if they are poor in salts. Neutral solutions of histons are precipitated by the alkaloid reagents and by solutions of ovalbumin and other proteins. In this group of bodies Bang includes goose-blood histon, thymus histon, scombron, and globin.

I have shown that edestan has all these reactions with the exception of the precipitation of the solution by heat in the presence of moderate quantities of neutral salts. This reaction could not be obtained with edestan as it is insoluble in water, and the

Bang: *Ztschr. physiol. Chem.*, 27, 463.

aqueous solution of its chloride gives a precipitate with a very little salt which is insoluble in stronger saline solutions.

The most important difference between these histons and edestan is that the former appear to be soluble in water when neutral, whereas neutral edestan is very insoluble in water, the reactions, which I have described, being given by aqueous solutions of its chloride. This combined acid, however, is present in such small proportion that it can be detected only in concentrated solutions by using very delicate litmus paper, so that it might easily be overlooked were its presence unknown. Bang gives no evidence that his solutions did not contain a similar proportion of acid and it seems probable that some of them at least did contain it, since the substances were extracted by dilute hydrochloric acid and the solutions made "neutral" presumably to litmus, this indicator being the one commonly employed by physiologists for such purposes. That any near relation exists between edestan and the bodies enumerated by Bang as histon is not probable, except in the case of globin, which seems to be more nearly related to edestan than to the histons since globin is a true protein substance, obtained from hemoglobin by the action of acids under conditions similar to those leading to the formation of edestan. With thymus histon and with scombron, it would seem that edestan and globin have little in common, since the two former yield little or no proteoses on pepsin digestion, whereas edestin yields such abundantly, and globin doubtless does the same.

From the facts now at our command it is evident that we have two different classes of bodies which conform pretty closely to the reactions characteristic of the histons. It is important to recognize this fact, since otherwise confusion will result if these two classes are not distinguished from one another, and protein derivatives produced by the acid used in preparing these substances may be regarded as actual constituents of the tissues.

#### SUMMARY.

By the action of water or very dilute solutions of acids, the globulin edestin is converted into a substance insoluble in saline solutions of moderate concentration.

This derivative of edestin is formed by hydrolysis, the amount formed being proportional to time and the concentration of the solution in hydrogen ions. In pure water less is formed in a given time than in water containing carbonic acid. More is

formed by a given quantity of hydrochloric acid than by an equivalent quantity of phosphoric acid, and by either of these acids much more is formed than by an equivalent of acetic acid.

This substance is the same as that designated as "albuminate" by Weyl, which is formed in greater or less amount in preparations of crystallized edestin made in the usual manner, and is without doubt the first product of the hydrolytic changes leading to the formation of the so-called acid albumin.

It is probable that the products insoluble in saline solutions which are formed from other globulins, originate from the same cause, and that these form a distinct class of hydrolytic derivatives of the native protein molecules.

For this derivative of edestin the name edestan is proposed.

The ultimate composition of edestan is the same, so far as can be determined by analysis, as that of edestin from which it originates.

Edestan forms salts with hydrochloric acid which react acid toward phenolphthalein to the full extent of the combined acid. One salt, having an acidity equivalent to 20 cc. of a centinormal solution per gram, is very sparingly soluble in water. It is this salt which forms the so-called "albuminate" found in edestin preparations. If edestan has a molecular weight near that of edestin, assumed to be about 14,500<sup>1</sup> this acidity would correspond to that of a trichloride, being just three times that of edestin monochloride and one and one-half times that of the bichloride.

Edestan is insoluble in water, far less soluble in solutions of potassium hydroxide than is edestin and insoluble in ammonia water, unless the solution of the latter is relatively very strong.

The aqueous solution of edestan chloride, when concentrated, reacts acid with litmus. It is precipitated by neutralization, the precipitate being soluble in strong ammonia, yielding a solution which is precipitated by ammonium chloride but not by sodium chloride.

The aqueous solution of edestan chloride gives a precipitate with nitric acid which dissolves on warming and reappears on cooling; a precipitate with ovalbumin solutions with the alkaloidal reagents and with sufficient mercuric chloride if its solution is concentrated. These reactions agree closely with those given

<sup>1</sup> See Osborne: *This Journal*, 21, 486 (1899); also the paper following.

by Kossel as characteristic of histons, but with the true histons edestan has little in common.

RESEARCH LABORATORY OF THE CONNECTICUT  
AGRICULTURAL EXPERIMENT STATION.

## THE BASIC CHARACTER OF THE PROTEIN MOLECULE AND THE REACTIONS OF EDESTIN WITH DEFINITE QUANTITIES OF ACIDS AND ALKALIES.

BY THOMAS B. OSBORNE.

Received September 28, 1901.

### I. INTRODUCTION.

#### *The Basic Character of the Protein Molecule.*

**T**HAT the proteins are ionized and highly reactive bodies is indicated by the rapidity with which they unite with both bases and acids, by the readiness with which, in many cases, they respond to changes in the ionization of their solutions, and also by the fact that they are, chemically, the most active constituents of protoplasm.

That they are neutral bodies, like the carbohydrates, is not in harmony with what is known of them.

Nevertheless, it appears to be generally assumed that a solution containing protein matter, which shows neither acid nor alkaline reaction with litmus, is chemically neutral.

Observations are on record which show that some protein solutions, when neutral to litmus, are acid to phenolphthalein and alkaline to lacmoid. It is also well known that a notable quantity of acid can be added to a protein solution before an acid reaction with tropaeolin, alizarine, or phloroglucin and vanillin appears.

The fact that acids combine with protein bodies is, therefore, well known, and, in making preparations of these substances, the necessity of removing such acids has long been recognized. This has been supposedly accomplished by adding potassium or sodium hydroxide or carbonate until the reaction with litmus becomes neutral. I am not aware that any one has offered any evidence, however, that by this procedure this object is fully accomplished. It is of importance, therefore, to know whether litmus can be used to determine the point when all combined acid has been converted into neutral salts of potassium or sodium and all the protein substance has been set free, or whether, as we know is the

case when tropaeolin or lacmoid is used as an indicator, more acid still remains combined.

Solutions in water of preparations of crystallized ovalbumin, in sodium chloride brine of excelsin, amandin, vignin, conglutin, glycinin, corylin, phaseolin and legumin, and in 75 to 90 per cent. alcohol of zein, gliadin and hordein,<sup>1</sup> which were either neutral or acid when tested with a strip of sensitive, neutral litmus paper, capable of showing distinctly the presence of 0.25 cc. of centinormal hydrochloric acid in 10 cc. of water, when made neutral to litmus, were, in every case, still acid towards phenolphthalein. With the exception of ovalbumin, these preparations had been made by the methods usually employed and had come in contact with no acid except that contained in the seeds from which they were obtained. The ovalbumin preparations were made both by Hopkins's and by Hofmeister's methods, the acidity of all of them being the same.

To render gram portions of these several protein preparations neutral to litmus required in a few cases not any, in most cases from 0.1 cc. to 1.5 cc. of, decinormal alkali; while to make the same 1-gram portions neutral to phenolphthalein required the further addition of from 0.7 to 1 cc. of decinormal alkali, except for legumin, which required 2 cc.

This reaction with phenolphthalein is sharp and definite, like that with strong mineral acids, and is independent of dilution, the same result being obtained in a volume of 10 cc. or in one of 100 cc.

The question now arises, whether complete neutralization of the combined acid is indicated by phenolphthalein or by litmus.

Preparations of edestin, which are neutral or acid to litmus, when suspended in water and made neutral to phenolphthalein by adding potassium hydroxide are not in any perceptible degree dissolved, but yield to the solution potassium salts of simple acids, which may be obtained therefrom by evaporation. When thus freed from these acids, the edestin immediately begins to dissolve if more alkali is added.

Edestin made neutral to phenolphthalein and dissolved in sodium chloride solution reacts distinctly alkaline towards litmus. This alkaline reaction is caused by the edestin itself and not by

<sup>1</sup> These protein bodies are described in Reports of the Connecticut Agricultural Experiment Station, 1890 to 1899; also Osborne: *Am. Chem. J.*, 13, 14 and 15; This Journal, 16, 17, 18, 19, 20 and 21; also "Die Proteide," etc., Heidelberg, 1897.

organic salts of the alkali, since such preparations yield a very small amount of ash, less than 0.05 per cent., which is neutral to both litmus and phenolphthalein.

Crystalline preparations of excelsin, obtained from the Brazil nut, *Bertholetia excelsa*, are undissolved when suspended in water and made neutral to litmus, but are completely dissolved when enough alkali, either potassium or its equivalent of ammonium hydroxide, is added to render the solution neutral to phenolphthalein. With less alkali, solution is not complete, the amount of excelsin dissolved depending upon the quantity of alkali added.

Likewise, preparations of legumin from the pea, horse bean, or vetch, when suspended in water, are completely dissolved only when enough potassium, or an equivalent of ammonium hydroxide is added to neutralize their acid reaction to phenolphthalein. It is highly improbable that excelsin and legumin can form soluble compounds with potassium which are neutral to phenolphthalein, and the fact that an exactly equivalent quantity of ammonium causes solution, is also evidence that this is not so, since a much larger proportion of ammonium hydroxide than of potassium hydroxide is required to dissolve edestin. Thus, 1 gram of a preparation of edestin, which was completely dissolved by 1 cc. of decinormal potassium hydroxide solution, was not entirely dissolved by 13 cc. of decinormal ammonium hydroxide. Furthermore, the proteins being very weak acids, it is scarcely possible that these form salts with potassium which are neutral to phenolphthalein. Certainly this is not the case with edestin, as the slightest excess of potassium hydroxide above that required to neutralize the combined acid at once turns phenolphthalein red.

Solutions of all the other protein bodies that I have examined, when similarly made neutral to phenolphthalein react decidedly alkaline with litmus.

From these facts it seems certain that the proteins are true bases, as I have previously pointed out,<sup>1</sup> and that they are not pseudoammonium bases, as Cohnheim and Krieger assume.<sup>2</sup>

## II. COMPOUNDS OF EDESTIN WITH ACIDS.

Since edestin, when neutral to phenolphthalein, is insoluble in

<sup>1</sup> Osborne: This Journal, 21, 486; Report of Connecticut Agricultural Experiment Station for 1899; also This Journal, 22, 402.

<sup>2</sup> Cohnheim and Krieger: *Ztschr. Biol.*, n. f., 22, 95.

water, it presents an opportunity for studying the nature of the acidity of its preparations, as obtained by the methods now used, that is offered by no other protein with which I am familiar. I have, therefore, subjected edestin to an extensive study, the details of which are given in the following pages.

This study appeared to be important, as edestin is a true protein substance, presenting all the essential characteristics of these bodies, so that the reactions into which it enters with bases and acids are, without doubt, to a large extent typical of those of the proteins in general.

### *1. The Degree of Acidity of Edestin Preparations.*

To neutralize to phenolphthalein the acid reaction of a sodium chloride solution of 1 gram of each of twenty different preparations of edestin made by all the various methods usually employed in preparing this substance, it was necessary to add from 0.85 to 1.5 cc. of decinormal potassium hydroxide solution. To neutralize eight of these solutions to litmus required from 0.2 to 0.5 cc., while the remaining twelve were neutral to litmus, the difference in the acidity of the several preparations measured by these two indicators being equal to from 0.85 to 1.10 cc. of decinormal alkali.

The degree of acidity towards phenolphthalein is very easily determined by direct titration, since the end reaction appears promptly. The same result is obtained by titrating the saline solution directly, by dissolving the preparation in an excess of alkali and titrating back, or by suspending the edestin in water in a stoppered bottle and adding the alkali until a red color appears. In the latter case the end-point is obtained more slowly, since the reaction takes place with one substance in the solid state.

### *2. The Nature of the Acids Combined with Edestin.*

Air-dried preparations of edestin, when suspended in water and treated with enough dilute potassium hydroxide solution to give a just perceptible alkaline reaction with phenolphthalein, do not dissolve, as already said, but form, on standing, dense deposits of disintegrated crystals, above which a voluminous flocculent layer of amorphous matter settles. Some samples, when thus treated, separate completely from the solution, leaving it clear and easily filtered; others form a milky, colloidal semi-solution which can-



not be filtered. These latter preparations, when suspended in 50 per cent. alcohol and neutralized to phenolphthalein with alkali, yield clear solutions which are easily filtered. The residue left on evaporating the filtrate and washings of the neutralized edestin, when dried at  $110^{\circ}$ , usually equals about 1.25 per cent. of the edestin, dried at the same temperature. The proportion of this residue obtained from several preparations was found to be as follows :

Preparation ..	4	7	9	10	11	12	13	15	18
Per cent.....	1.30	1.05	1.27	1.21	1.40	1.26	1.41	1.15	1.44
				1.26	1.41			1.17	

In order to find the composition of these residues, 75 grams of preparation 19<sup>1</sup> were exhausted with large quantities of 75 per cent. alcohol until the final washings left, on evaporation, no notable quantity of solids. The total residue left by evaporating the whole of these washings weighed 0.2833 gram, equal to 0.38 per cent. of the protein. Its solution in water was made neutral to phenolphthalein by 3.4 cc. of decinormal potassium hydroxide solution, and yielded a precipitate, chiefly protein, weighing 0.1159 gram. The filtrate from this, when evaporated, left a residue weighing 0.1674 gram, of which 0.0133 gram was potassium that had been added in neutralizing the solution. Deducting this, we find that only 0.1541 gram of non-protein matter had been removed by washing 75 grams of edestin. On ignition, a residue of mineral matter remained, weighing 0.0600 gram, from which again should be deducted 0.0133 gram, corresponding to the potassium contained in the 3.4 cc. of decinormal solution added, so that the total mineral matter removed by exhaustive washing from the 75 grams of edestin amounted to only 0.0467 gram, or 0.06 per cent. The absence of more than traces of soluble mineral matter remaining in this sample of edestin having thus been demonstrated, it was suspended in pure water, and 90 cc. of decinormal potassium hydroxide solution, diluted with much water, was gradually added, which sufficed to exactly neutralize the mixture to phenolphthalein. After being shaken in a closed flask for some hours, the undissolved edestin was filtered out and washed by decantation with alcohol of about 65 per cent. by volume, applied in six successive portions of

<sup>1</sup> This was obtained by treating hemp seed with 3 per cent. brine heated to  $60^{\circ}$  and cooling the clear extract. The protein, which separated wholly in octahedral crystals, therefore constitutes a preparation of crude edestin.

1 liter each. The filtrate and washings were separately evaporated and left residues, when dried at  $110^{\circ}$ , which weighed as follows :

TABLE I.—SOLUBLE MATTER FORMED BY NEUTRALIZING EDESTIN 19 WITH POTASSIUM HYDROXIDE.

		Gram.
1st	aqueous filtrate.....	0.2542
1st	one liter 65 per cent. alcohol .....	0.1225
2d	" " 65 " " " .....	0.0680
3d	" " 65 " " " .....	0.0750
4th	" " 65 " " " .....	0.0725
5th	" " 65 " " " .....	0.0480
6th	" " 65 " " " .....	0.0308
Total .....		0.6710

These residues were united and extracted with strong alcohol, in which a part dissolved. The part soluble in alcohol was also soluble in water, forming a yellow solution which required 0.3 cc. of decinormal hydrochloric acid to neutralize it to litmus, and 0.7 cc. to phenolphthalein.

When this alcoholic solution was evaporated and the residue burned at a low temperature, alkaline vapors were evolved in small amount.

The matters soluble and insoluble in strong alcohol weighed respectively 0.1514 and 0.6173 gram, and when analyzed were found to contain the following substances :

TABLE II.—COMPOSITION OF THE POTASSIUM SALTS FORMED BY NEUTRALIZING A CRUDE PREPARATION OF CRYSTALLIZED EDESTIN 19 WITH POTASSIUM HYDROXIDE.

	Part soluble in strong alcohol.		Part insoluble in strong alcohol.	
	Gram.	Per cent.	Gram.	Per cent.
Organic matter.....	0.0825	54.42	0.1429	23.15
Potassium carbonate.....	0.0400	26.38	0.0600	9.72
Potassium sulphate.....	0.0200	13.33	0.0766	12.41
Potassium chloride.....	0.0052	3.43	0.2750	44.55
Potassium phosphate.....	.....	....	0.0235	3.74
Sodium chloride.....	.....	....	0.0091	1.47
Undetermined and loss....	0.0037	2.44	0.0302	4.96
	0.1514	100.00	0.6173	100.00

The sum of the mineral matters contained in the two portions is 0.5433 gram, and had the following composition :

TABLE III.—COMPOSITION OF TOTAL INORGANIC SALTS FORMED BY NEUTRALIZING THE CRUDE PREPARATION OF CRYSTALLIZED EDESTIN 19 WITH POTASSIUM HYDROXIDE.

Potassium carbonate.....	0.1000	18.40
Potassium sulphate.....	0.0966	17.81
Potassium chloride.....	0.2802	51.54
Potassium phosphate.....	0.0235	4.32
Sodium chloride.....	0.0091	1.67
Undetermined and loss.....	0.0339	6.26
	0.5433	100.00

From these figures we find that the greater part of the soluble substances formed by neutralizing this preparation consists of potassium salts of mineral acids and that 60 per cent. of the potassium in these salts is present as chloride.

We also find that alcohol dissolves a large proportion of the organic matter which consists largely of potassium salts of one or more organic acids, since the quantity of potassium carbonate formed after igniting is equal to about one-half the combustible matter. The sum of this latter and the potassium carbonate is 0.1225 gram, of which 0.0211 gram is potassium and 0.1014 gram organic. From this a maximum mean molecular weight of 188 can be calculated, which shows that no considerable part of the potassium carbonate is formed from potassium compounds of protein.

Owing to the exhaustive washing to which this preparation had been subjected before neutralization, it is improbable that this organic matter was an admixed impurity, nor was it a free organic acid insoluble in water, because the solution of its potassium salt remained clear on adding a little hydrochloric acid, showing the organic acid to be readily soluble in water.

We must, therefore, conclude that this organic matter consists of one or more of the organic acids of the seed, which had combined with the edestin.

In confirmation of these results, this experiment was repeated, with sample 20, prepared from a sodium chloride extract of hemp seed, which had been neutralized to litmus with potassium hydroxide, and dialyzed until the edestin had precipitated in crystals. This precipitate was redissolved in 10 per cent. sodium chloride brine, heated to 50°, the solution diluted with three volumes of water at the same temperature, filtered perfectly clear and cooled at 12°. The beautifully crystallized deposit which

separated was thoroughly washed, first with 1 per cent., then with 0.5 per cent. sodium chloride solution, and finally with 50 per cent. alcohol until all the salt was removed. This method of washing with dilute salt solution and alcohol was necessary, because on washing with water alone a large part of the preparation dissolved, the reason for which is later explained.

Thirty grams of the air-dry preparation were suspended in pure, freshly-boiled water, and 24 cc. of decinormal potassium hydroxide solution, likewise diluted with water, were added. The mixture, perfectly neutral to phenolphthalein, was allowed to stand some time, filtered, and the insoluble edestin thoroughly washed with dilute alcohol.

The filtrate and washings were evaporated, the residue dried at 110°, weighed and analyzed with the following results:

TABLE IV.—COMPOSITION OF THE POTASSIUM SALTS FORMED BY NEUTRALIZING A RECRYSTALLIZED PREPARATION OF EDESTIN 20 WITH POTASSIUM HYDROXIDE.

	Gram.	In per cent. of the inorganic matters.
Organic matters.....	0.0315	....
Potassium carbonate.....	0.0083	5.7
Potassium sulphate.....	0.0095	6.5
Potassium chloride .....	0.1081	73.9
Sodium chloride.....	0.0108	7.4
Undetermined and loss.....	0.0095	6.5
Total .....	0.1777	100.0

These figures in general confirm those previously given, but show a larger proportion of potassium chloride and a smaller proportion of organic salts and sulphate. This is doubtless the result of the recrystallization, whereby this preparation, 20, was finally separated from a solution containing a much smaller proportion of negative ions other than those of chlorine than that existing in the solution from which 19 was crystallized.

As already stated, a part of many preparations of edestin dissolves in water when the associated salts are mostly washed out. In order to determine whether or not this solubility is due to a difference in the nature of the acids united to the soluble and to the insoluble parts, 30 grams of preparation 20 were exhausted with pure water and the filtered solution was neutralized with 10.6 cc. of decinormal potassium hydroxide solution, whereby the edestin was wholly precipitated. The clear filtrate and washings

from this precipitate were evaporated, the residue dried at 110° and analyzed, with results as follows:

TABLE V.—COMPOSITION OF THE POTASSIUM SALTS FORMED BY NEUTRALIZING THE PART OF THE EDESTIN PREPARATION WHICH WAS SOLUBLE IN WATER.

	Gram.	In per cent. of the inorganic matters.
Organic matters .....	0.0902	....
Potassium carbonate.....	0.0021	1.4
Potassium sulphate .....	0.0096	6.6
Potassium chloride .....	0.0721	49.8
Sodium chloride.....	0.0585	40.4
Undetermined and loss .....	0.0025	1.8
Total .....	0.2350	100.0

The presence of sodium chloride, which forms so large a part of these salts, is undoubtedly due to incompletely washing the original preparation, which had been recrystallized several times from dilute brine and, in order that the water-soluble edestin compound should not be removed from it, had been washed first with 0.5 per cent. brine and then with 50 per cent. alcohol. The inorganic residue obtained in a similar experiment, described on page 49, contained only 11.41 per cent. of sodium chloride, which shows that in the present case this is to be regarded as an accidental contamination and not as a product of neutralization.

The potassium hydroxide used for neutralizing the edestin was equivalent to 0.0791 gram of potassium chloride, of which salt 0.0721 gram appears in the analysis, even after calculating all the other acids as potassium salts. From this, it is evident that the water-soluble edestin was mostly combined with hydrochloric acid. It is to be noted that all the added alkali, in this case, was recovered, whereas in the experiments first described only 70 per cent. was found in solution. This is doubtless due to the fact that in these first experiments the acid neutralized was largely contained within the body of the crystals,<sup>1</sup> and, as these crystals did not dissolve when neutralized, the potassium salts which formed within them were washed out with great difficulty. In this last experiment the edestin was wholly dissolved at the time the alkali was added, and consequently the potassium salts that formed were easily separated from it.

<sup>1</sup> Under the microscope the greater part of the undissolved edestin is seen to consist of fragments of crystals, most of which are of relatively considerable size, so that potassium salts formed within these fragments are necessarily extracted with difficulty.

The part of preparation 20 which did not dissolve on treating with water, was next suspended in pure, boiled water and neutralized to phenolphthalein, by carefully adding 16.6 cc. of decinormal potassium hydroxide solution. After standing some time, the solution was filtered and the undissolved edestin thoroughly washed with 75 per cent. alcohol. The filtrate and washings, when evaporated, left a residue which, when dried at  $110^{\circ}$ , was analyzed with the following results :

TABLE VI.—COMPOSITION OF THE POTASSIUM SALTS FORMED BY NEUTRALIZING THE PART OF THE EDESTIN PREPARATION WHICH WAS INSOLUBLE IN WATER.

	Gram.	In per cent of the inorganic matters.
Organic matters.....	0.0574	....
Insoluble mineral matter....	0.0067	5.8
Potassium carbonate.....	0.0121	10.5
Potassium sulphate.....	0.0117	10.1
Potassium chloride.....	0.0710	61.5
Sodium chloride.....	0.0085	7.4
Undetermined and loss.....	0.0055	4.7
	0.1729	100.0

In this experiment, 75 per cent. of the potassium added was recovered, of which 76 per cent. is chloride and 11 per cent. sulphate.

In the similar experiment, to be described on page 50, 85 per cent. of the potassium added was recovered, of which 47.6 per cent. was chloride and 52.4 per cent. sulphate. Since the present experiment yielded so small a proportion of sulphate, it is evident that the insolubility of edestin in water is not simply due to combined sulphuric acid, but, as we shall later show, is chiefly due to the *greater proportion* of acid combined with the soluble part.

To make a preparation which, when neutralized, should yield only chloride, 3,000 grams of hemp-seed meal were extracted with 9 liters of brine heated to  $60^{\circ}$  and containing 3 per cent. of almost chemically pure sodium chloride. The filtered extract was cooled to  $8^{\circ}$  and allowed to stand over night, until the large crop of crystals had been deposited. These crystals were then collected on a filter, washed once with water, redissolved in 1 liter of sodium chloride brine, the solution filtered perfectly clear, heated to  $55^{\circ}$ , diluted with three volumes of water at the same temperature, and rapidly cooled to  $0^{\circ}$ .

The crystalline deposit which separated was suspended in water, brought on a filter, and this process repeated until all the edestin soluble in water was washed out. The three portions of washings first obtained were almost protein-free, the fourth contained nearly one-half of the original preparation, the fifth much less, and the sixth very little.

To the fourth portion enough pure sodium chloride was added to form a 10 per cent. solution. This caused at first an abundant precipitate, most of which dissolved when more of the salt passed into the solution, which was then filtered and dialyzed for forty hours, whereby its salt content was reduced to 2 per cent., and the edestin was precipitated in beautiful crystals. These were filtered out, washed with 50 per cent. alcohol and finally with absolute alcohol and dried over sulphuric acid, giving 37 grams of a perfectly crystallized, dazzlingly white preparation, 22, which was mostly soluble in pure water, and wholly soluble in sodium chloride solution.

To neutralize to phenolphthalein, a quantity of this preparation corresponding to 1 gram of the water and ash-free substance, 1.22 cc. of decinormal potassium hydroxide solution was required, corresponding to an acidity which, as we shall see later, is that of a mixture containing a small proportion of the water-insoluble, with a large proportion of the water-soluble, edestin compound.

Twenty grams of this preparation, air-dry, were then treated with 600 cc. of pure water, 220 cc. of centinormal potassium hydroxide solution added, and the voluminous precipitate filtered out and washed with 250 cc. of water. The filtrate and washings, when evaporated, left a residue, which had the following composition :

TABLE VII.—POTASSIUM SALTS FORMED BY NEUTRALIZING EDESTIN, PREPARATION 22.

	Gram.	In per cent. of the inorganic matters.
Organic matters .....	0.0185	....
Potassium carbonate.....	0.0020	1.19
Potassium sulphate.....	0.0065	3.89
Potassium chloride .....	0.1398	83.51
Sodium chloride.....	0.0191	11.41
	<hr/> 0.1859	<hr/> 100.00

Although the free edestin had been only superficially washed, we find over 85 per cent. of the added potassium to be contained

in these salts, 95 per cent. of which is present as chloride. The proportion of sulphate to chloride in these salts is less than 2 molecules of the former to 100 of the latter. Although this preparation was nearly free from sulphate, nevertheless a perfectly pure chloride was not obtained in this way.

Twenty grams of that part of the edestin, which, as already described, did not dissolve in water, were suspended in 600 cc. of water and neutralized by adding 12 cc. of decinormal potassium hydroxide solution. The solution filtered from the undissolved edestin, together with the washings, was evaporated and the residue analyzed with the following results :

TABLE VIII.—COMPOSITION OF POTASSIUM SALTS FORMED BY NEUTRALIZING THAT PART OF THE EDESTIN PREPARATION WHICH WAS INSOLUBLE IN WATER.

	Gram.	In per cent. of the inorganic matters.
Organic matters.....	0.0340	...
Potassium carbonate.....	none	...
Potassium sulphate.....	0.0479	49.6
Potassium chloride.....	0.0373	38.7
Sodium chloride.....	0.0079	8.2
Undetermined and loss .....	0.0034	3.5
	0.1305	100.00

In this residue we have a larger proportion of sulphate than in any previously analyzed. We shall later show edestin sulphate to be less soluble in water than the corresponding chloride, and, for this reason, it is probable that the edestin sulphate had accumulated in the fraction insoluble in water. Whether edestin sulphate is a constituent of the seed or results from sulphates contained in the sodium chloride and in the river water in which the solutions were dialyzed was not determined, but the latter seems probable, because, before its final precipitation, this substance was wholly soluble in water.

From these results it appears that edestin preparations, obtained by cooling or by dialyzing saline solutions, usually consist of mixtures of several compounds of the protein with acids, the proportion of the different compounds formed depending upon the degree of acidity of the solution and the nature of the negative ions which are present when the edestin crystallizes out.

Owing to the difficulty of obtaining edestin chloride free from sulphate, it seemed possible to obtain the sulphates free from other acid compounds.



Four kilograms of hemp-seed meal were accordingly extracted with 15 per cent. ammonium sulphate solution, the extract saturated with the same salt, and the protein thus precipitated was filtered out and dissolved in the dilute sulphate solution which resulted on adding water. The clear solution, when dialyzed, deposited relatively large octahedral crystals, which, when washed with water and alcohol and dried, weighed 440 grams, preparation 23.

Fifty grams of this preparation were suspended in water and made exactly neutral to phenolphthalein by adding 45 cc. of decinormal potassium hydroxide solution, diluted with much water. As the neutral edestin did not separate from the solution in a condition to be filtered, an equal volume of alcohol was gradually added. The clear filtrate and washings then obtained were evaporated and the residue analyzed with the following results:

TABLE IX.—COMPOSITION OF THE POTASSIUM SALTS FORMED BY NEUTRALIZING EDESTIN, PREPARATION 23.

	Gram.	In per cent. of the inorganic matters.
Organic matters.....	0.2269	....
Potassium carbonate .....	0.0480	18.98
Potassium sulphate .....	0.1956	77.34
Potassium chloride .....	0.0066	2.61
Undetermined and loss.....	0.0027	1.07
	<hr/> 0.4798	<hr/> 100.00

The effect of substituting sulphate for chloride in extracting edestin is plainly shown by these figures, over 75 per cent. of the recovered potassium being sulphate and less than 3 per cent. chloride. Of the potassium added in neutralizing, 66 per cent. was recovered in the above salts, which agrees well with the 70 per cent. obtained in the previously described experiments in which the edestin crystals did not dissolve but fell into relatively large fragments on neutralizing.

In order to convert, if possible, edestin sulphate into chloride, 50 grams of this preparation, 23, were suspended in 70 per cent. alcohol and 50 cc. of decinormal potassium hydroxide solution added. The edestin thus made neutral was filtered out, dissolved in 500 cc. of 10 per cent. sodium chloride solution and carefully mixed with an equal volume of the same brine containing 50 cc. of decinormal hydrochloric acid. The solution was filtered clear, dialyzed, the crystalline precipitate washed with water, until all

the soluble edestin was removed, the residue suspended in water, neutralized to phenolphthalein, and the potassium salts produced, analyzed with the following results:

TABLE X.—COMPOSITION OF THE POTASSIUM SALTS FORMED BY NEUTRALIZING EDESTIN CHLORIDE OBTAINED FROM EDESTIN SULPHATE.

	Gram.	In per cent. of the inorganic matters.
Organic matters.....	0.0192	....
Potassium carbonate.....	0.0016	2.01
Potassium sulphate.....	0.0130	16.31
Potassium chloride.....	0.0587	73.65
Undetermined and loss.....	0.0064	8.03
	0.0989	100.00

These figures show that over 82 per cent. of the potassium was recovered as chloride and less than 16 per cent. as sulphate.

The many experiments here described can leave no doubt that the acidity of edestin preparations is chiefly caused by hydrochloric and sulphuric acids and that by neutralizing to litmus only a part of the combined acids is removed.

As to the nature of the organic acid, which was present in all the salts described, no information has been obtained, too little being present to make its identification possible.

To determine whether this organic acid was in fact an acid combined with the protein substance or was a product resulting from local overaction of the alkali on the edestin molecule, I extracted hemp-seed meal with 10 per cent. sodium chloride solution containing enough baryta to cause the extract to be just neutral to litmus and then precipitated the edestin from the filtered extract by dialysis against distilled water.

The crystalline product thus obtained was thoroughly washed with water, dissolved in brine, again precipitated by dialysis and extensively washed with water. The moist product was then suspended in water, made neutral to phenolphthalein by adding very dilute potassium hydroxide solution, filtered out and redissolved in 10 per cent. sodium chloride brine. The resulting solution was mixed with an equal volume of the same brine, containing hydrochloric acid equivalent to the potassium hydroxide previously used for neutralizing and the solution dialyzed. The crystalline precipitate was filtered out, washed and neutralized as before and the entire process again repeated. The three solutions

filtered from the three successive edestin precipitates caused by neutralization were evaporated and the residues analyzed.

TABLE XI.—COMPOSITION OF SALTS RESULTING FROM THREE SUCCESSIVE NEUTRALIZATIONS OF AN EDESTIN PREPARATION.

	I. Per cent.	II. Per cent.	III. Per cent.
Potassium carbonate.....	7.4	5.1	0.8
Potassium sulphate.....	4.4	2.6	23.0
Potassium chloride.....	82.8	80.6	71.3
Sodium chloride.....	.....	5.2	3.6
Undetermined.....	5.4	6.5	1.3
	100.0	100.0	100.0

These figures show that the organic potassium compound practically vanished after the third precipitation, and therefore it is highly probable that this is a salt of an organic acid previously combined with the edestin and not a product of the action of the alkali upon the protein molecule.

### 3. *The Proportion of Acid Combined with Edestin.*

On page 42, I have shown that all of a large number of edestin preparations are, without exception, acid to phenolphthalein, and that many of them are also acid to litmus. Some of these preparations are decidedly more acid than others. Most of the more acid contain more substance soluble in water than those less acid. Some, however, of the most acid are wholly insoluble in water. All of these latter were prepared from solutions containing ammonium *sulphate* and, when neutralized with potassium hydroxide, yielded chiefly potassium *sulphate*, whereas the others containing substance soluble in water, yielded, on thus neutralizing, chiefly potassium *chloride*.

The difference between the degree of acidity of the part of the preparation which is soluble in water and of that which is insoluble therein is, however, marked. In upwards of a hundred trials, I have invariably found the acidity of the part soluble in water to be equivalent to very nearly 1.4 cc. of decinormal acid per gram of the dissolved edestin, while that of the insoluble part was but half as great, provided the preparation tested was made without using ammonium sulphate. As an illustration of this, the following experiments may be given.

A quantity of an edestin preparation was made by cooling a warm sodium chloride extract of hemp seed and repeatedly

recrystallizing the precipitate from warm, dilute salt solution. The substance was then washed by decantation with water. The first, second and third solutions decanted contained no edestin, owing to the salts present in them, but the fourth and fifth contained some.

It was necessary to add 0.8 cc. of decinormal potassium hydroxide solution to 10 cc. of the fourth decantation in order to obtain a neutral reaction with phenolphthalein, while exactly twice as much was required by 20 cc. By evaporating, and drying the residue at  $110^{\circ}$ , it was found that 10 cc. contained 0.5777 gram of edestin, so that 1 gram of the soluble edestin neutralized 1.39 cc. of decinormal alkali. Similarly, 25 cc. of the fifth washings, containing 0.5320 gram, required for neutralization 0.7 cc. of decinormal alkali, equal to 1.32 cc. per gram.

Eighteen grams of that part of the original preparation which did not dissolve on exhausting with water, when suspended in water, was made exactly neutral to phenolphthalein by 12 cc. of decinormal alkali, or 0.66 cc. per gram,—that is, by just one-half the quantity of alkali required by the soluble part.

Further, another quantity of edestin from which all the compounds soluble in water had been removed and which, when subsequently dried at  $110^{\circ}$ , weighed 21.27 grams, required when freshly washed and not dried 16.6 cc. of decinormal alkali to render it neutral to phenolphthalein, or 0.78 cc. of decinormal alkali for each gram of protein.

On page 51 the method is described by which a part of preparation 23, yielding chiefly sulphate when neutralized, was converted into a crystalline preparation, yielding chiefly chloride. The product thus obtained was exhausted with water until nothing more was removed from it, and that part which remained undissolved was uniformly suspended in water and 10 cc. drawn out and mixed, in a stoppered bottle, with 1.5 cc. of decinormal potassium hydroxide solution and phenolphthalein. A clear red solution was formed at once, which required 0.95 cc. of decinormal hydrochloric acid for neutralization, showing 0.55 cc. of the alkali to have been neutralized by the acid combined with the edestin. By evaporating and drying the residue at  $110^{\circ}$ , it was found that the 10 cc. contained 0.8152 gram of edestin, from which it is seen that 1 gram of the compound insoluble in water ad an acidity equal to 0.68 cc. of decinormal acid. Two other

similar trials gave exactly the same result. Ten cc. of the mixture were also added to 10 cc. of 20 per cent. sodium chloride solution, phenolphthalein added and then decinormal potassium hydroxide solution until a slight pink color formed, for which 0.55 cc. was likewise required.

Edestin preparations suspended in water and treated with an insufficient quantity of hydrochloric acid to dissolve them, yield solutions which have an acidity equal to 1.4 cc. of a decinormal solution per gram of dissolved protein.

From all these facts it is clear that the acidity of the edestin chloride, which is soluble in water, is twice that of the part which is insoluble therein.

If the edestin molecule contains two atoms of sulphur, its weight must be about 7,250, or a multiple of this. If the acidity of the water-soluble edestin is equal to 1.4 cc. of decinormal acid per gram and if one molecule of acid unites with one of edestin to form a water-soluble compound, the molecular weight of edestin would be 7,129. But, since the water-soluble edestin is twice as acid as the water-insoluble, the former must contain at least two molecules of acid, so that the molecular weight of edestin must be about 14,258, or a multiple of this.

We thus have, in these two acid compounds, a rational explanation for the fact, first observed by Ritthausen, that a part of most edestin preparations is soluble in pure water, while the remainder is insoluble therein. That this was due to a chemical difference between these two parts was most probable, although preparations showing this behavior consisted wholly of crystals having apparently the same form.

That these two compounds of different composition, as well as the other salts and the free edestin, should crystallize in the same form is to be expected, since the form of the crystal is determined by the protein molecule, the weight of which is enormous compared with that of the one or two molecules of acid combined with it. The same condition occurs with the compounds of hemoglobin, the crystals of carbon monoxide hemoglobin being isomorphous to those of oxyhemoglobin. The same isomorphism also occurs among minerals of high molecular weight, as shown by Penfield and Foote,<sup>1</sup> who state: "In tourmaline we have an isomorphous relation of a very peculiar nature, for in the acid

<sup>1</sup> Penfield and Foote. *Am. J. Sci.*, 8, 122 (1899).

$H_2Al_2(BOH)_2Si_2O_5$ , the nine hydrogens may be replaced to a large extent by the trivalent metal aluminum or by the bivalent metals magnesium and iron without any decided change in crystalline form. This leads to the consideration of a certain phase of isomorphism which, as it seems to us, has not been considered with sufficient care, namely, the mass effect of complex radicals in influencing or controlling crystallization."

If such be the case with a mineral acid containing but (41)<sub>n</sub> atoms we certainly should expect the mass influence of a molecule containing approximately (2,000)<sub>n</sub> atoms to be all-controlling.

#### 4. *Reactions of Edestin With Larger Quantities of Acid.*

It has long been known that protein substances combine with acids, and it is a common practice to determine the amount of acid combined with products of gastric digestion. In these products, however, the combined acid is chiefly held by proteoses and peptones, bodies that are known to have more basic properties than the native proteins from which they originate.<sup>1</sup> Panormoff<sup>2</sup> has recently described definite compounds of ovalbumin with different acids, but these contain a much larger proportion of acid than the salts of edestin just described, and are doubtless compounds of a different order (see preceding paper).

I have, however, obtained evidence that edestin also enters into definite reaction with similar large quantities of acid.

A study of the action of water and acids upon edestin has shown that a hydrolytic change is effected in the edestin molecule, whereby a more basic derivative is formed, which shows an entirely different behavior with alkalies and salt solutions from that exhibited by the original, unchanged edestin. It is probable, therefore, that these more acid compounds are not salts of edestin, but salts of more basic derivatives, which form intermediate steps in a series of changes leading to the so-called "acid albumin." Whether or not these changes are common to the other "native proteids" I have not as yet ascertained with certainty, but it is probable that they are. Gram portions of the air-dry preparations of edestin, 11, 12, and 13, were suspended in water and decinormal hydrochloric acid gradually added, until a drop of the solution, evaporated on porcelain, showed with tropaeolin a distinct

<sup>1</sup> Cf. Chonheim and Krieger: *Ztschr. Biol.*, n. 1., 22, 95.

<sup>2</sup> Panormoff: *J. russ. phys.-chim. Ges.*, 31, 556.

red reaction, which in each case appeared with 12 cc. The tests were then repeated by adding to each solution 11 cc. of acid and afterward increasing this quantity by successive additions of 0.2 cc. By testing with tropaeolin after each such addition, it was found that one gram of 11 had reacted with 11.2 cc., 12 with 11.5 cc., and 13 with 11.3 cc. Calculating these figures for the preparation dried at 110° and ash-free, and adding to this the acid originally contained in them, we find that 11 had reacted with 13.9 cc., 12 with 13.7 cc., and 13 with 14.1 cc., which corresponds almost exactly to a compound of 1 molecule of edestin with 20 molecules of acid, assuming this protein to have a molecular weight of approximately 14,500, or, in other words, to exactly ten times the quantity of acid required to form a soluble compound with 1 gram of edestin.

Strong evidence of a definite reaction with about 10 molecules of acid was obtained by testing with potassium nitrite and iodide. A series of five 1-gram portions of 11 were suspended in water in small, glass-stoppered bottles, and to them were respectively added 4 cc., 5 cc., 6 cc., 6.5 cc., and 7.5 cc. of decinormal hydrochloric acid and then to each 7.5 cc. of a solution of soluble starch, containing 1 per cent. of potassium iodide and 1 per cent. of potassium nitrite.

The portion containing 7.5 cc. of acid became blue throughout within five minutes, the color first appearing at the top of the solution; that with 6.5 cc. began to turn blue at the top within a minute and a half, and became wholly blue in twelve minutes; that with 6 cc. showed a trace of blue on the surface after five minutes, which, even after thirty minutes, was very slight and limited to the upper surface; that with 5 cc. showed a trace of blue on the surface after fifteen minutes, which was still slight after an hour and a half; that with 4 cc. behaved like that with 5 cc., except that, on adding the nitrite solution, a large, permanent precipitate formed, whereas all the other solutions remained very nearly clear. On standing over night, in the stoppered bottles, the difference between the various portions was much more pronounced, for from those to which 4, 5, and 6 cc. of acid had been added, an opaque yellowish jelly had separated, above which was a clear blue jelly, whereas the portion with 6.5 cc. formed a thin blue jelly containing but little of the

opaque substance, and presented a wholly different appearance from those with 6 cc. and less.

From this it would appear that this edestin preparation combined with the hydrogen ions contained in 6 cc. of decinormal hydrochloric acid more firmly than with those contained in the larger quantities. If we add the acid originally combined with the edestin, we may conclude that the hydrogen ions equivalent to 7 cc. of the acid were more firmly combined with the protein than those contained in the larger quantities.

#### 5. *Solubility of Edestin in Hydrochloric Acid.*

Having found that edestin forms a water-soluble salt with hydrochloric acid, I undertook to determine the amount dissolved by definite quantities of this acid. To do so, it was necessary to make a preparation which should be as neutral as possible to phenolphthalein, free from any of the hydrolytic derivative of edestin, mentioned on page 56, and as free as possible from ash.

This is accomplished by extracting oil-free hemp-seed meal with 3 per cent. sodium chloride brine, previously heated to 60°, to which is added enough saturated baryta solution to render the extract neutral to litmus, the requisite quantity being determined by a preliminary experiment with 100 grams of the meal. It is important to avoid an excess of baryta, since otherwise, compounds of edestin with basic constituents of the seed seem to be formed, which are difficult to get rid of afterwards.

The hot extract is strained on coarse cloth and the residue pressed. The very turbid extract is thrown on large paper filters and allowed to stand at rest for about two hours. During this time a part of the extract filters through and the residue settles in the funnels so that about two-thirds of the solution can be drawn off as a turbid liquid, which, however, contains but little suspended matter. This is filtered by suction on thick felts of filter pulp on perforated porcelain plates placed in large funnels, all being previously washed with 3 per cent. salt solution heated to 70°. By thus filtering, this part of the extract may be readily obtained perfectly clear and the filter be washed with hot dilute salt solution, within two hours, 2 liters being passed through each filter. During this time, most of the residual extract passes through the paper filters, so that what remains can be rejected without serious loss. The clear extracts are united in a large



glass-stoppered bottle and allowed to stand over night and cool to 5° or less. The edestin separates as a dense deposit of crystals, from which the solution is siphoned and thrown away, since very little more can be obtained from it by further dilution and cooling.

The crystallized edestin is next dissolved in 10 per cent. salt solution, best by adding a volume of 20 per cent. solution equal to that of the mother-liquor remaining with the crystals after siphoning off the greater part. Enough 10 per cent. salt solution is then added so that the solution contains about 8 per cent. of edestin, since stronger solutions, under the subsequent treatment, do not, as a rule, yield well crystallized products. This saline solution of edestin is heated to 50° and gradually diluted with two volumes of water, at the same temperature, whereby a perfectly clear solution results. By again cooling to 5° the edestin is re-crystallized. By repeating this process a very pure crystalline product is obtained, which is again dissolved in enough 10 per cent. sodium chloride brine, free from carbonic acid, to make an 8 per cent. solution of edestin. An aliquot part of this solution is neutralized to phenolphthalein with decinormal sodium hydroxide solution, and the quantity of alkali necessary to neutralize the whole is determined. The edestin solution is then heated to 50° in a glass-stoppered jar, and twice its volume of carbonic acid-free water at the same temperature and containing 4 or 5 cc. more than the calculated quantity of the decinormal alkali is gradually added. The mixture, carefully protected from carbonic acid, is allowed to cool during the night to 5°, the nearly clear solution siphoned off, and the crystalline precipitate collected on a piece of Schleicher & Schüll's thick, hardened filter-paper placed on a perforated plate. The precipitate, consisting of crystals, is very quickly sucked almost dry and washed two or three times with 1 per cent. sodium chloride solution, cooled to 0°, and free from carbonic acid, then three times with carbonic acid-free water, ten times with 70 per cent. alcohol, and many times with absolute alcohol, all the wash-water and alcohol being at 0°. It is necessary that the washing should be complete and the dehydration with absolute alcohol thorough, so that on drying over sulphuric acid no water should be left after the alcohol has gone off, which would convert a part of the edestin into the insoluble edestan.

Owing to the physical state of the crystalline edestin, the fil-

tration, washing and dehydration of 50 to 100 grams can be accomplished within twenty minutes. Preparations made in this way were either neutral or very nearly neutral to phenolphthalein, completely soluble in salt solution, contained not more than 0.02 to 0.03 per cent. of ash, and consisted of fine powders, free from lumps, which can be uniformly suspended in water and almost instantly dissolved by the requisite quantity of acid, alkalies, or salts.

It is very difficult to keep the edestin from combining with minute quantities of carbonic acid, since during the final filtration and washing, a brief exposure to the air is unavoidable, without employing elaborate and cumbersome apparatus. As a result, from 1 to 2 cc. of centinormal alkali were required to neutralize one gram of most preparations thus made.

This process is given in detail, as I was unable to prepare edestin suitable for the experiments next to be described, until I had worked out this method of preparation in all its details.

A series of gram portions of preparation 28, made as above described, was suspended in glass-stoppered bottles, in enough water to make a final volume of 20 cc. with the acid subsequently added. To one portion no acid was added, to the next 2 cc. of centinormal hydrochloric acid, to the next 3 cc., and then 1 cc. more to each succeeding portion, up to 14 cc.

A second, exactly similar series, was also made, commencing with 6 cc.

After frequently shaking the contents of the bottles for about two hours, they were allowed to stand at rest for two hours longer until the suspended matter had practically all deposited. From each solution 10 cc. were drawn out with a pipette, the acidity of each such 10 cc. determined with centinormal potassium hydroxide solution, and then all separately evaporated to dryness on a water-bath and the residues dried to constant weight at 110°. In this way the results given in the following table were obtained:

TABLE XII.—EDESTIN DISSOLVED BY A CENTINORMAL SOLUTION OF HYDROCHLORIC ACID.

	0.0 cc.	2 cc.	3 cc.	4 cc.	5 cc.	6 cc.	7 cc.	8 cc.
I....	0.0104	0.0082	0.0504	0.0526	0.0718	0.1400	0.1876	0.2576
II....	.....	.....	.....	.....	.....	0.1460	0.1702	0.2458
	9 cc.	10 cc.	11 cc.	12 cc.	13 cc.	14 cc.	$\frac{\text{HCl}}{100}$	
I....	0.3362	0.4358	0.5850	0.6816	0.7650	0.8406	gram.	
II....	0.3378	0.4336	0.5636	0.6590	0.7350	0.8080	gram.	

The acidity of the solutions and of the residues of Series I was determined by titration with centinormal alkali and phenolphthalein, with the following results :

TABLE XIII.—DISTRIBUTION OF ACID BETWEEN THE DISSOLVED AND UNDISSOLVED EDESTIN IN TERMS OF CENTINORMAL ACID.

0.0 cc.	2 cc.	3 cc.	4 cc.	5 cc.	6 cc.	7 cc.	8 cc.
0.0 cc.	0.0 cc.	0.0 cc.	0.0 cc.	0.5 cc.	1.8 cc.	2.6 cc.	3.9 cc.
1.3 cc.	2.9 cc.	3.6 cc.	4.5 cc.	5.0 cc.	4.25 cc.	4.4 cc.	4.4 cc.
1.3 cc.	2.9 cc.	3.6 cc.	4.5 cc.	5.5 cc.	6.05 cc.	7.0 cc.	8.3 cc.
9 cc.	10 cc.	11 cc.	12 cc.	13 cc.	14 cc.	$\frac{\text{HCl}}{100}$	
5.0 cc.	6.8 cc.	8.6 cc.	10.6 cc.	12.2 cc.	13.6 cc.	Dissolved.	
4.0 cc.	3.6 cc.	2.4 cc.	1.9 cc.	1.0 cc.	0.8 cc.	Undissolved.	
9.0 cc.	10.4 cc.	11.0 cc.	12.5 cc.	13.2 cc.	14.4 cc.	Total.	

The degree of acidity of the dissolved and undissolved edestin,—that is, the amount of centinormal alkali neutralized by 1 gram of the edestin chloride contained in the solution and residues of each of these portions,—is given in the following table :

TABLE XIV.—THE ACIDITY CORRESPONDING TO ONE GRAM OF THE DISSOLVED AND UNDISSOLVED EDESTIN CHLORIDE OF TABLE XIII.

0.0 cc.	2 cc.	3 cc.	4 cc.	5 cc.	6 cc.	7 cc.	8 cc.
0.0 cc.	0.0 cc.	0.0 cc.	0.0 cc.	6.0 cc.	11.8 cc.	13.0 cc.	14.4 cc.
1.5 cc.	3.3 cc.	4.3 cc.	5.4 cc.	6.4 cc.	6.8 cc.	6.4 cc.	7.0 cc.
9 cc.	10 cc.	11 cc.	12 cc.	13 cc.	14 cc.	$\frac{\text{HCl}}{100}$	
14.3 cc.	15.1 cc.	14.0 cc.	15.1 cc.	15.6 cc.	16.0 cc.	Dissolved.	
7.3 cc.	8.0 cc.	8.0 cc.	9.4 cc.	8.5 cc.	.....	Undissolved.	

From this table it appears that 1 gram of the substance in the solutions to which from 7 to 12 cc. of acid had been added, neutralized nearly the same quantity of centinormal alkali as that calculated for a compound of one molecule of edestin with 2 molecules of hydrochloric acid, assuming edestin to have a molecular weight of about 14,500, namely 13.8 cc.

Since the amount of edestin in many of these portions was small, most of these determinations are only approximately correct. As already stated, one-half of each of the solutions in these experiments was drawn out with a pipette and the acidity and quantity of dissolved matter was determined as shown above. In order to more accurately determine the acidity of the dissolved edestin by using a larger proportion of substance, the remainder of those solutions of Series I to which from 7 to 13 cc. had been added, was decanted from the undissolved edestin, united and

neutralized by 20 cc. of centinormal potassium hydroxide solution. By evaporating, and drying the residue at  $110^{\circ}$ , this solution was found to contain 1.4459 grams of edestin, corresponding to an acidity equal to 13.8 cc. of centinormal alkali per gram, or exactly that above calculated. Similarly, the remaining solutions from Series II were neutralized by 25 cc. of centinormal alkali and contained 1.6941 gram of edestin, corresponding to an acidity equal to 14.7 cc. per gram. From these facts it is evident that the substance brought into solution by the acid has the acidity of a bichloride.

The acidity of the undissolved edestin increases with each increase in added acid, until in the portion containing 6 cc. it reaches 6.8 cc. per gram, which corresponds to the formation of a monochloride. With the larger quantities of added acid, this acidity of the undissolved edestin remains nearly constant, although a slight increase is apparent. This excess of acidity above that of the monochloride is caused by the formation of a small proportion of a hydrolytic derivative of edestin, which I have designated *edestan*. Edestan has a higher acid-combining power than edestin and forms with acid a salt which is very sparingly soluble in water. The formation and properties of edestan are described in detail in the preceding paper.

Table XII shows that a small quantity of edestin is apparently dissolved by the water to which no acid had been added as well as by that to which 2 cc. were added. This small quantity is due to a little suspended matter, drawn off with the solution, and is not to be considered as dissolved edestin. In the portions containing 3, 4, and 5 cc. of acid, some edestin appears to be dissolved, but as these, in contrast with the others, were opalescent and neutral, it is most probable that they were colloidal or false solutions caused by edestin bichloride, formed by a local overexcess of acid, which was subsequently reprecipitated on coming into contact with uncombined edestin.

By 6 cc., some edestin was dissolved, but the lower acidity of this portion indicates that the whole of this was not brought into solution by the acid. From 6 cc. upward, a uniformly increasing quantity of edestin passed into solution, until only an insignificant amount remained undissolved by 14 cc. If edestin has a molecular weight of about 14,500 and forms an insoluble chloride with 1 molecule of hydrochloric acid, about 6 cc. of centinormal hydro-

chloric acid should convert 1 gram of an air-dry preparation into this chloride. In Table XII it is seen that the edestin does not dissolve with less than 6 cc. of acid. Strictly, none should dissolve with less than 7 cc., but as this preparation had an acidity of about 1 cc. per gram, the hydrogen ions causing this ought, in so dilute a solution, to contribute equally with those of the hydrochloric acid in reacting with the edestin, and hence a corresponding quantity should be dissolved.

That this soluble acid compound of edestin contains twice as many molecules of acid as the insoluble acid compound, is shown by the rate at which the acidity of the solution of this substance increased in comparison with the rate at which the acid was added in these experiments. Thus, the solution produced by 10 cc. of acid neutralized 1.80 cc. more alkali than that produced by 9 cc., although but 1 cc. more acid had been added; that with 11 cc. also neutralized 1.8 cc. more alkali than that with 10 cc.; that with 12 cc. neutralized 2 cc. more alkali than that with 11 cc.; that is, after the whole of the edestin was converted into the insoluble chloride, each molecule of acid subsequently added brought into solution another molecule of acid which had been previously combined with the edestin as an insoluble chloride.

If edestin has a molecular weight of about 14,500, each cubic centimeter of centinormal acid in excess of 7 cc. should dissolve 0.1450 gram. The quantity actually dissolved by each cubic centimeter of acid in excess of 7 cc. falls considerably short of this, chiefly owing to the formation of the more basic derivative, edestan, mentioned on page 56.

Edestan forms sparingly soluble salts with larger quantities of acid than does edestin. In these experiments about 8 per cent. of edestan was formed and consequently the amount of edestin dissolved per cubic centimeter of acid was less than that calculated.

From these results it would appear that edestin, like a true base, enters into ionic reactions with hydrochloric acid. That a weak base should enter into such complete reaction with hydrochloric acid is due to the dilution of the solution, for if its molecular weight is 14,500, a solution containing 5 per cent. of this substance is nearly equivalent to a  $\frac{1}{1000}$  normal solution.

This method of determining the quantity of edestin brought into solution by hydrochloric acid was next applied to prepara-

tions of the chlorides obtained by the methods formerly employed for the preparation of edestin. The only difference in the manipulation of these experiments consisted in filtering the acid solutions on small felts of washed paper pulp, with help of a pump, and washing each filter and residue with 20 cc. of water.

As a part of each of these preparations was soluble in water,—that is, consisted of water-soluble acid compounds of edestin,—the amount dissolved by water alone was deducted from that obtained from each portion to which acid had been added, the difference being the quantity of edestin dissolved by the given quantity of acid. The results thus obtained are given in Table XV.

TABLE XV.—EDESTIN CHLORIDE DISSOLVED BY CENTINORMAL HYDROCHLORIC ACID.

Preparation.	1 cc.	2 cc.	3 cc.	4 cc.	5 cc.	6 cc.
No. 2. I.....	0.1041	0.2306	0.3291	0.4726	0.5426	0.6301
II.....	.....	0.2451	0.3279	.....	0.5301	0.6025
No. 4. ....	0.0920	0.2300	0.3260	0.4425	0.5681	0.6380
No. 11. I.....	0.1194	0.2540	0.3679	0.4445	0.4950	0.5085
II.....	0.0738	0.1968	0.3398	0.4498	0.5369	0.6068
No. 15. I.....	0.0916	0.2235	0.3250	0.4332	0.5528	0.5762
II.....	0.1015	0.2291	0.3455	0.4445	0.5365	.....
No. 20. I.....	0.1295	0.2655	0.3761	0.4790	0.5115	.....
II.....	0.1140	.....	0.3484	.....	.....	.....
III.....	0.0870	0.2095	0.3335	0.5125	0.6035	.....
IV.....	0.0745	0.2055	0.2935	0.4030	0.4625	.....

AVERAGE OF THE ABOVE FIGURES.

Preparation.	1 cc.	2 cc.	3 cc.	4 cc.	5 cc.	6 cc.
No. 2 .....	0.1041	0.2409	0.3285	0.4726	0.5364	0.6163
No. 4 .....	0.0920	0.2300	0.3260	0.4425	0.5681	0.6380
No. 11 .....	0.0966	0.2254	0.3539	0.4472	0.5160	0.5577
No. 15 .....	0.0966	0.2263	0.3352	0.4388	0.5446	0.5762
No. 20 .....	0.1012	0.2268	0.3379	0.4648	0.5258	.....

Although notable irregularities occur among these figures, the results, on the whole, are as uniform as perhaps we could expect them to be under the conditions of the experiments. It is to be noted that the greater differences are found for the smaller and for the larger quantities of acid employed, that is, in those cases where slight differences in manipulation would naturally cause the greatest variation in the results.

In the table only 60 per cent. of the edestin is shown to be dissolved by the acid employed. This is due to the fact that the

remaining 40 per cent. consisted of moisture, ash, acid compounds of edestin which were soluble in water, and a little of the hydrolytic derivative, edestan, which is insoluble in salt solutions. It was necessary, therefore, to add only about 6 cc. of acid in order to bring into solution all the edestin monochloride contained in each preparation.

The following table gives the average weight, in grams, dissolved per cubic centimeter of centinormal hydrochloric acid in each portion to which the designated quantity of acid was added.

TABLE XVI.—EDESTIN CHLORIDE DISSOLVED PER CC. OF CENTINORMAL HYDROCHLORIC ACID SOLUTION.

Preparation.	1 cc.	2 cc.	3 cc.	4 cc.	5 cc.	6 cc.
No. 2 .....	0.1041	0.1204	0.1095	0.1181	0.1073	0.1027
No. 4 .....	0.0920	0.1150	0.1087	0.1106	0.1136	0.1063
No. 11 .....	0.0966	0.1127	0.1179	0.1118	0.1032	0.0920
No. 15 .....	0.0920	0.1131	0.1117	0.1097	0.1089	0.0960
No. 20 .....	0.1012	0.1164	0.1126	0.1162	0.1052	0.1022

These results, while not so accordant as those obtained with pure and neutral edestin, are nevertheless in harmony with them.

To find what effect the nature of the acid combined with the edestin would have upon the solubility of edestin in hydrochloric acid, a similar series of determinations was made with preparation 13, which consisted mostly of edestin sulphate, having been obtained by saturating an extract with ammonium sulphate and dialyzing the solution of the precipitate so produced. The results obtained were as follows:

TABLE XVII.—EDESTIN SULPHATE DISSOLVED BY CENTINORMAL HYDROCHLORIC ACID.

Preparation.	0.0 cc.	2 cc.	3 cc.	4 cc.	5 cc.	6 cc.	7 cc.	8 cc.
13	0.0000	0.0150	0.0420	0.0825	0.1500	0.3070	0.4435	0.4776
		9 cc.	10 cc.	11 cc.	12 cc.			
		0.5616	0.6860	0.7521	0.8378			

From these figures we see that very little edestin dissolves with less than 6 cc. of hydrochloric acid, that is, it does not dissolve until the sulphate has been converted into the chloride. Above 7 cc. solution proceeds at about the same rate as with edestin chlorides. It is evident that the combined sulphuric acid contributes but little to the solution of the edestin, since the sulphate corresponding to the bichloride is insoluble in water.

Plate I shows at a glance the solubility of these several preparations of edestin and its salts.

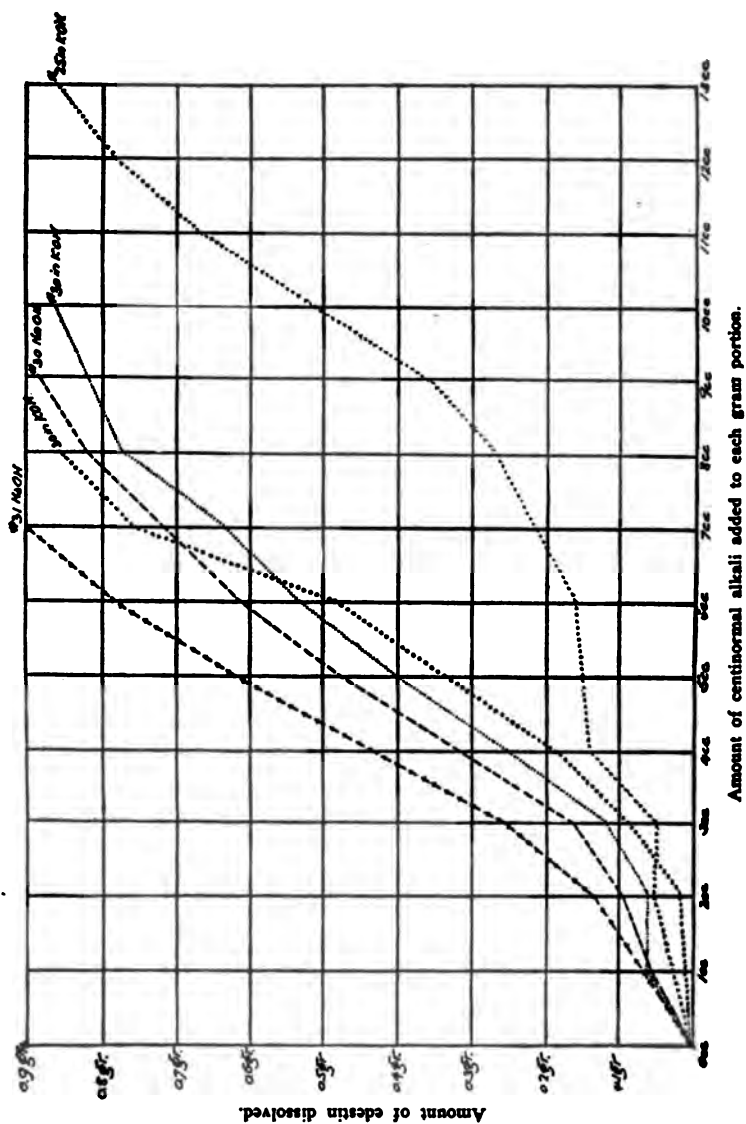


PLATE I.—SOLUBILITY OF EDESTIN IN CENTINORMAL HYDROCHLORIC ACID.



6. *Solubility of Edestin in Sulphuric Acid.*

Preparation 23, which I have shown on page 51 to be nearly pure edestin sulphate, required nearly ten times as much decinormal sulphuric acid for solution as edestin chloride required of decinormal hydrochloric acid. It was, therefore, necessary to use a decinormal acid in carrying out experiments similar to those just described, but in the following table the amount of acid is stated in terms of a centinormal solution, in order to avoid possible confusion on comparing the figures with those of the preceding tables. This preparation had an original acidity equal to 10 cc. of a centinormal solution per gram and, as none of it dissolved in water, this amount of acid is added to that applied to the preparation, so that all the acid present with which the edestin could react is here taken into account.

TABLE XVIII.—EDESTIN SULPHATE DISSOLVED BY CENTINORMAL SULPHURIC ACID.

<i>Amount in Grams of Dissolved Edestin Sulphate.</i>							
	10 cc.	20 cc.	30 cc.	40 cc.	50 cc.	60 cc.	70 cc.
No. 23.	0.0000	0.0705	0.1750	0.4355	0.6245	.....	0.9075
	0.0000	0.0510	0.2280	0.4740	0.6950	0.8680	0.9088
<i>Amount of Edestin Sulphate Dissolved Per cc. of Centinormal H<sub>2</sub>SO<sub>4</sub> Solution.</i>							
No. 23.	0.0000	0.0035	0.0058	0.0109	0.0125	.....	0.0130
	0.0000	0.0026	0.0076	0.0118	0.0139	0.0145	0.0130
<i>Acidity of the Solution of Edestin Sulphate in cc.</i>							
No. 23.	0.0	3.0	6.0	18.0	33.0	...	67.0
	0.0	2.0	8.5	21.5	37.5	57.0	64.0
<i>Acidity of the Solution Per Gram of Dissolved Edestin in cc.</i>							
No. 23.	0.0	43.0	35.3	41.3	52.9	...	73.7
	0.0	39.2	37.3	45.4	54.0	65.7	71.0

From these figures it is plain that a much larger quantity of sulphuric acid is required to dissolve a given amount of edestin than of hydrochloric acid. The edestin sulphate corresponding to the bichloride is insoluble in water. Whether the soluble compound formed with a sufficient quantity of sulphuric acid is a salt of edestin or whether a hydrolytic derivative of edestin is first produced which forms soluble compounds with the larger quantity of sulphuric acid, was not ascertained, but the behavior of edestin with hydrochloric acid would indicate this to be the case.

7. *The Solubility of Edestin in Phosphoric and Acetic Acids.*

Phosphoric acid reacts with edestin as a monobasic acid, in accordance with its dissociation into the ions  $H$  and  $H_2PO_4$ .

One gram of the air-dry preparation, suspended in 6 cc. of water, was completely dissolved when treated with 14 cc. of a centinormal solution of phosphoric acid. With 13 cc., 0.8920 gram was dissolved, which is very nearly the calculated quantity, namely, 0.9230 gram.

Acetic acid likewise reacts with almost the calculated amount of edestin, since I found that 13 cc. of a centinormal solution dissolved 0.8804 gram.

Both these acids dissolve somewhat more edestin than does an equivalent quantity of hydrochloric acid, 13 cc. of a centinormal solution of which dissolved about 0.7770 gram. This difference appears to be due to the formation of different proportions of the more basic edestan, as the following experiments indicate. To each of 3 gram portions of edestin suspended in 6 cc. of water, were respectively added 14 cc. of a centinormal solution of each of these acids. After standing for about two hours at  $25^\circ$ , the acid in each was exactly neutralized, and an equal volume of 20 per cent. sodium chloride solution was added. The amount of the insoluble edestan present in the portion with hydrochloric acid was 0.1786 gram, in that with phosphoric acid 0.1484 gram, and in that with acetic acid 0.0565 gram. These results are approximately in accord with the degree of ionization of these acids and appear to explain the relative incompleteness of the reactions with the respective acids.

8. *The Solubility of Edestin in Nitric Acid.*

Nitric acid dissolves edestin chloride in nearly the same proportion as does hydrochloric acid, but a larger quantity of the former acid is required to dissolve the neutral edestin at about  $20^\circ$  than of the latter. At  $35^\circ$  one air-dry gram of neutral edestin equal to 0.9300 gram dried at  $110^\circ$ , was completely dissolved by 14 cc. of centinormal nitric acid, but by 12 cc. at this temperature much remained undissolved. At  $20^\circ$ , 1 gram was completely dissolved by 20 cc., all but a very few milligrams by 19 cc., while with 18 cc. much remained undissolved.

This quantity of acid is in such close agreement with that required for the formation of a trinitrate that it strongly suggests

that such is formed, but it is not safe to assume this without other evidence to confirm it.

That a compound with 2 molecules of nitric acid should exist which is more soluble in warm than in cold water, is in harmony with the known behavior of this acid with proteoses, some other protein substances and the histons.

A more extended study of this question is necessary, and I shall take it up as soon as possible.

### III. COMPOUNDS OF EDESTIN WITH ALKALIES.

It is well known that protein substances react with alkalies as well as with acids, in which respect they closely resemble the purin bases, which, as pronounced bases, form salts with acids and are also able, like weak acids, to form with bases definite compounds, of which the silver salt is one of the best known, since it is used for the separation of these bodies from their ammoniacal solution.

Many unsuccessful attempts have been made to obtain definite compounds of the proteins with bases, especially with the heavy metals. The chief reason that these failed probably lies in the fact that the small quantity of acid which these substances still contain when their solutions are made neutral to litmus has been overlooked, and also to the fact that salts of the heavy metals are hydrolytically dissociated to such an extent as to make it difficult or impossible to maintain suitable conditions for the formation of definite metallic compounds with the proteins.

The experiments next to be described show that edestin enters into definite reaction with potassium and sodium.

#### 1. *Solubility of Edestin in Sodium Hydroxide Solution.*

Preparation 31, which was strictly neutral to phenolphthalein, was used to determine the solubility of edestin with definite quantities of sodium hydroxide, in a manner similar to that employed in determining the solubility of edestin with definite quantities of hydrochloric acid.

Gram portions of the air-dry preparation were suspended, in glass-stoppered bottles, in enough water, free from carbonic acid, to make 20 cc. with the alkali solution to be afterwards added. To the first, 2 cc., to the second, 3 cc., and so on up to 7 cc., of centinormal sodium hydroxide solution were added. After agitating frequently for an hour, the solutions were allowed to stand

at rest for another hour, during which time the undissolved matter settled, leaving the solution nearly clear. From each portion 10 cc. were drawn out with a pipette, evaporated to dryness, and the residues dried to constant weight at 110°. The amount dissolved by each quantity of alkali added is shown in the following table:

TABLE XIX.—AMOUNT OF EDESTIN 31 DISSOLVED BY A CENTINORMAL SOLUTION OF SODIUM HYDROXIDE.

2 cc.	3 cc.	4 cc.	5 cc.	6 cc.	7 cc.	$\frac{\text{NaOH}}{100}$
0.1244	0.2564	0.4358	0.6086	0.7834	0.8990	gram dissolved.

The amount, in grams of edestin dissolved per cubic centimeter with each quantity of alkali added, was the following:

TABLE XX.—AMOUNT OF EDESTIN 31 DISSOLVED PER CC. OF CENTINORMAL SODIUM HYDROXIDE.

2 cc.	3 cc.	4 cc.	5 cc.	6 cc.	7 cc.	$\frac{\text{NaOH}}{100}$
0.0622	0.0855	0.1090	0.1217	0.1306	0.1283	gram dissolved.

These figures show that the amount dissolved per cubic centimeter steadily rises, until with 6 and 7 cc. it reaches a maximum. This is due to the difficulty with which all of the soluble sodium edestin is separated from the relatively large quantity of edestin remaining undissolved in those portions to which the smaller amounts of alkali had been added, since the great extent of surface presented by the fine crystalline powder strongly adsorbs the soluble sodium edestin and also, to the indiffusibility of the substance, since any sodium edestin formed within the solid particles is removed with difficulty. With increasing quantities of alkali the proportion of undissolved edestin diminishes and the proportion dissolved per cubic centimeter correspondingly increases until it reaches a quantity but little less than that calculated for a complete reaction between one molecule of edestin and one of sodium hydroxide.

Another series of gram portions of preparation 30, 1 gram of which had an acidity requiring 2 cc. of centinormal sodium hydroxide solution for neutralization to phenolphthalein, was treated in the same way as the preceding and the following amounts were found to be dissolved:

TABLE XXI.—AMOUNT OF EDESTIN 30 DISSOLVED BY CENTINORMAL SODIUM HYDROXIDE SOLUTION.

1 cc.	2 cc.	3 cc.	4 cc.	5 cc.	6 cc.	7 cc.*	8 cc.	9 cc.	$\frac{\text{NaOH}}{100}$
0.0490	0.0940	0.1636	0.3208	0.4800	0.6060	0.7120	0.8188	0.8782	$\frac{\text{gram}}{\text{gram}}$ dissolved.

In this case the effect of the carbonic acid contained in this preparation is plainly manifested, since 9 cc. of the alkali were required to dissolve the same amount that 7 cc. dissolved of the perfectly neutral preparation 31. The small quantity appearing to be dissolved by 1 and 2 cc. consisted mostly of suspended matter unavoidably drawn off with the solution. The agreement between these results and those obtained in the first experiment is best shown by the solubility curves given in Plate II.

2. *Solubility of Edestin in Potassium Hydroxide Solution.*

Preparation 28, 1 gram of which required 2 cc. of centinormal alkali for neutralization to phenolphthalein, was treated with a centinormal solution of potassium hydroxide in the way described for experiments with sodium hydroxide. Table XXII shows the weight in grams dissolved by the several quantities of alkali.

TABLE XXII.—AMOUNT OF EDESTIN 28 DISSOLVED BY CENTINORMAL POTASSIUM HYDROXIDE SOLUTION.

1 cc.	2 cc.	3 cc.	4 cc.	5 cc.	6 cc.	7 cc.	8 cc.	$\frac{\text{KOH}}{100}$
0.0000	0.0150	0.0938	0.1944	0.3294	0.4772	0.7592	0.8500	gram dissolved.

The amount dissolved per cubic centimeter above 2 cc. was as follows :

TABLE XXIII.—AMOUNT DISSOLVED PER CC. OF CENTINORMAL POTASSIUM HYDROXIDE.

3 cc.	4 cc.	5 cc.	6 cc.	7 cc.	8 cc.	$\frac{\text{KOH}}{100}$
0.0938	0.0972	0.1098	0.1193	0.1518	0.1417	gram dissolved.

In this, as in the experiments with sodium hydroxide, the proportion of dissolved edestin increased as the proportion of undissolved edestin diminished, the amount dissolved by 8 cc. being nearly equal to that calculated for a complete reaction between equal numbers of molecules of each substance. The somewhat higher figure found for 7 cc. is doubtless due to a slight error of manipulation, as indicated by the rise in the curve given in Plate II, showing the results of this experiment.

Another similar series of gram portions of edestin 30, treated with centinormal potassium hydroxide in the same way as 28 had been treated, gave the following results :

TABLE XXIV.—AMOUNT OF EDESTIN 30 DISSOLVED BY CENTINORMAL POTASSIUM HYDROXIDE SOLUTION.

1 cc.	2 cc.	3 cc.	4 cc.	5 cc.	6 cc.	7 cc.	8 cc.
0.0586	0.0574	0.1146	0.2496	0.3984	0.5220	0.6292	0.7726
		9 cc.	10 cc.	$\frac{\text{KOH}}{100}$			
		0.8120	0.8558	gram dissolved.			

These results are nearly the same as those obtained with preparation 28, the amount dissolved by less than 7 cc. being slightly more than in the first series, while that dissolved by more than 7 cc. is slightly less.

Assuming that true solution begins only with 3 cc., we have the following quantities, in grams, dissolved per cubic centimeter with each quantity of alkali added :

TABLE XXV.—EDESTIN 30, DISSOLVED PER CC. OF CENTINORMAL POTASSIUM HYDROXIDE SOLUTION.

3 cc.	4 cc.	5 cc.	6 cc.	7 cc.	8 cc.	9 cc.	10 cc.	$\frac{\text{KOH}}{100}$
0.1146	0.1248	0.1328	0.1305	0.1258	0.1288	0.1160	0.1060	gram dissolved.

As this table shows, with from 5 to 8 cc., the amount dissolved per cubic centimeter is about 15 milligrams less than that calculated for a complete reaction between equal numbers of molecules of the protein and alkali. The rate at which this preparation dissolved is more uniform than that at which 28 dissolved, the effect of adsorption being much less in these experiments with 30 than in those with 28. Probably this is due to the fact that the crystals of 30 were much larger than those of 28, and therefore a much smaller surface was exposed by the former on which the soluble edestin could be adsorbed than by the latter preparation.

A similar experiment with another preparation, 25, was also made with the following results.

TABLE XXVI.—AMOUNT OF EDESTIN 25, DISSOLVED BY A CENTINORMAL SOLUTION OF POTASSIUM HYDROXIDE.

2 cc.	3 cc.	4 cc.	6 cc.	8 cc.	9 cc.	10 cc.	12 cc.	13 cc.	$\frac{\text{KOH}}{100}$
0.0058	0.0048	0.1380	0.1588	0.2694	0.3594	0.5044	0.7790	0.8678	{ gram dissolved.

This preparation, which, when first precipitated, was perfectly neutral to phenolphthalein, became so acid, after washing and drying without precautions to exclude carbonic acid, the necessity of which was not recognized at the time the preparation was made, that 4 cc. of centinormal alkali were required to neutralize 1 gram of it.

From the solutions, to which 2 and 3 cc. of alkali had been added, the insoluble edestin settled out, leaving the solution very nearly clear and showing no opalescence whatever. Unlike 28, this preparation at first dissolved slowly, only 0.02 gram more being dissolved by 6 cc. than by 4 cc. but from 6 cc. upwards,

solution proceeded at nearly the same rate as in the other experiments.

That more edestin was not dissolved by the potassium carbonate first formed with the carbonic acid previously combined with the edestin, is due to the slight degree of hydrolytic dissociation occurring with this salt, an insufficient amount of hydroxyl ions being formed to cause a noticeable solution of the edestin.

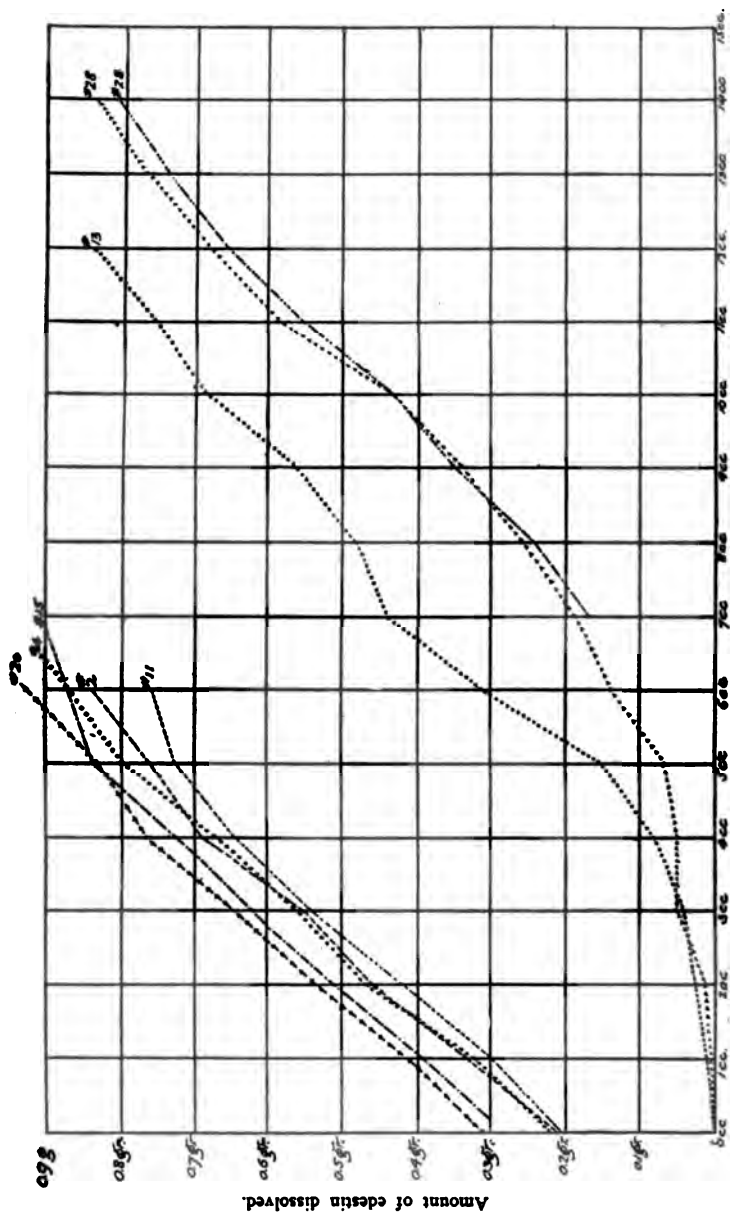
Plate II, page 74, shows the relations of these experiments with alkalis to one another and makes very evident the effect of the small amount of carbonic acid which some of the preparations contained.

Preparations consisting of mixtures of edestin mono- and bichlorides are completely dissolved when suspended in water and an excess of centinormal potassium or sodium hydroxide solution is added, equivalent to about 7 cc. per gram of edestin. The proportion of such edestin preparations dissolved by a smaller excess of alkali cannot be determined, as the solution from which the undissolved edestin chloride deposits on standing is milky and cannot be filtered because supersaturated with free edestin arising from the water-soluble bichloride.

Solutions of sodium or potassium edestin become turbid after several hours and gradually deposit a part of the protein from the supersaturated solution thus formed. Solutions of calcium or barium edestin, which are formed only in the presence of a much larger proportion of these inorganic bases, are far less stable than those of sodium or potassium edestin and soon deposit a large proportion of the dissolved protein, together with a considerable part of the mineral base. Probably the substance which separates from solutions of these compounds is a derivative of edestin, but this has not been determined.

Solutions of sodium or potassium edestin are precipitated by extremely small amounts of neutral salts, but are unaffected by non-electrolytes, such as sugar or alcohol, unless the latter is added in large quantity. The precipitate thus produced is readily and completely dissolved by adding a sufficient quantity of sodium chloride. In this saline solution these compounds of edestin show the properties of globulin.

Towards salts, potassium and sodium edestin behave like edestin bichloride. In the absence of salts, the aqueous solutions



Amount of centinormal hydrochloric acid added to each gram portion.  
 PLATE II.—SOLUBILITY OF EDESTIN IN CENTINORMAL ALKALI.



of all these compounds are clear and in no way resemble opalescent colloidal solutions. The solutions produced by strong sodium chloride brine are likewise clear.

### 3. *Solubility of Edestin in Sodium Carbonate Solution.*

Each one of a series of gram portions of edestin 30 was suspended, in a stoppered bottle, in water enough to make a final volume of 20 cc. with the decinormal sodium carbonate solution to be afterwards added. After adding the amounts of decinormal sodium carbonate solution stated in the table and frequently shaking, the solutions were allowed to stand until the suspended matter had settled. As the portions containing 0.2 cc., 0.4 cc., and 0.6 cc. settled slowly, these were filtered through pure paper, and 10 cc. of each solution of the entire series were evaporated, the residue dried at 110°, and the following quantities were found to have been dissolved:

TABLE XXVII.—AMOUNT OF EDESTIN DISSOLVED BY A DECINORMAL SODIUM CARBONATE SOLUTION:

0.2 cc.	0.4 cc.	0.6 cc.	1.0 cc.	1.4 cc.	1.8 cc.	2.2 cc.	2.4 cc.	2.5 cc.	$\frac{\text{Na}_2\text{CO}_3}{10}$
0.0090	0.0376	0.0580	0.2202	0.4722	0.6036	0.7510	0.8160	0.8618	gram.

Very little edestin is dissolved by less than 0.6 cc. of the sodium carbonate solution, doubtless because of the small amount of carbonic acid contained in this preparation. Above 0.6 cc. the edestin dissolved at a nearly uniform rate, as shown by the following table, which gives the amount in grams dissolved in each portion per 0.1 cc. in excess of 0.6 cc.

Thus the amount dissolved by 1 cc. was 0.2202 gram or 0.1622 gram more than was dissolved by 0.6 cc., therefore one-fourth of this quantity, 0.0405 gram, was dissolved by each 0.1 cc. in excess of 0.6 cc.

TABLE XXVIII.—EDESTIN DISSOLVED PER 0.1 CC. OF DECINORMAL SODIUM CARBONATE SOLUTION IN EXCESS OF 0.6 CC.

1 cc.	1.4 cc.	1.8 cc.	2.2 cc.	2.4 cc.	2.5 cc.	$\frac{\text{Na}_2\text{CO}_3}{10}$
0.0405	0.0518	0.0455	0.0433	0.0421	0.0423	gram dissolved.

From these figures it is seen that the amount of edestin dissolved is proportional to the amount of sodium carbonate added in excess of 0.6 cc.

A larger proportion of sodium carbonate is required to neutralize a preparation of edestin chloride than of potassium hydroxide. Five grams of preparation 3 were suspended in water, 5 cc.

of decinormal sodium carbonate solution added, the mixture shaken for some time, the edestin filtered out, and to the filtrate and washings 5 cc. of decinormal hydrochloric acid added. The solution was then boiled, cooled, and neutralized to phenolphthalein by 3.8 cc. of potassium hydroxide solution, from which it is evident that only 3.8 cc. of the sodium carbonate solution had been neutralized by the combined acid of the edestin chloride, which contained sufficient acid to neutralize 5 cc. of *caustic alkali*.

Whether the edestin is dissolved by sodium carbonate solely in consequence of the hydrolytic dissociation of this salt, or whether this salt acts also as a solvent, after the manner of neutral salts such as sodium chloride, requires further investigation into the relations of globulins to neutral salts, which is now in progress in this laboratory.

#### IV. CONCLUSIONS.

1. The proteins are basic bodies and enter into ionic reactions with acids with which they form true salts.
2. Preparations of native proteins, as usually obtained from solutions slightly acid or neutral to litmus, are salts of the basic protein substance.
3. The acid of these salts can be separated from those proteins that are insoluble in water, by making them neutral to phenolphthalein with potassium or sodium hydroxide. The acid combined with the protein can then be identified in the aqueous solution, by filtering out the insoluble protein, evaporating the solution and analyzing the alkaline salts thus obtained.
4. Preparations of edestin, made by the methods commonly employed, contain chiefly chlorides, when crystallized from sodium chloride solutions,—chiefly sulphates, when crystallized from a solution containing ammonium sulphate. The salts of edestin which crystallize out are those of the negative ions present in the solution, the predominating salt being that of the negative ion most abundant at the time of crystallization.
5. Edestin preparations, as usually made from sodium chloride solutions, generally dissolve to a considerable extent when washed with pure water. The part that dissolves is twice as acid toward phenolphthalein as the part that remains undissolved.
6. The degree of acidity of the part insoluble in water is equal to that of a compound of 1 molecule of edestin with 1 of hydrochloric acid, assuming that the former has a molecular weight

of about 14,500, which is twice as great as the simplest one that can be calculated from its analysis, if there are 2 atoms of sulphur in its molecule.

Edestin, therefore, forms salts corresponding to a mono- and bichloride.

7. The crystals of edestin, as well as those of its different salts, are, so far as has been determined, isomorphous, the mass influence of the protein molecule being so great as to prevent the small amount of combined acid from effecting a change in crystalline form. In this respect, edestin behaves like hemoglobin, the compounds of which with oxygen and with carbonic acid are also isomorphous.

8. The free base edestin, when suspended in pure water, is dissolved by nearly the calculated quantity of hydrochloric acid required for a complete reaction between 1 molecule of edestin and 2 of hydrochloric acid. On adding the acid in successive small quantities, no solution takes place, until one-half the required amount has been added. On adding the second half of the acid, solution takes place at a rate proportional to the amount of acid added. The acidity of the solution obtained with the second half of the acid increases at twice the rate at which the acid is added, in accordance with the conversion of an insoluble monochloride produced by the first half of the acid into a soluble bichloride formed by the second half.

9. Somewhat more than the calculated quantity of hydrochloric acid is required to dissolve a given quantity of edestin, because a more basic hydrolytic derivative of edestin, sparingly soluble in water, is formed by the hydrogen ions set free by hydrolytic dissociation of the chloride.

10. Since solutions of edestin bichloride do not appear to be precipitated by hydrolytic dissociation, it is probable that edestin hydroxide may be formed and remain in solution under the conditions of the experiments tried.

11. Edestin sulphates are less soluble than the corresponding chlorides and, consequently, preparations obtained from solutions containing ammonium sulphate are not soluble in water. Ten times more sulphuric acid is required to dissolve a given quantity of edestin than of hydrochloric acid. Definite compounds with sulphuric acid have not yet been obtained.

12. Hydrochloric acid dissolves more nearly the calculated

quantity of edestin than does acetic acid, since the latter, being less ionized than the former, produces, in a given time, only one-third as much of the more basic hydrolytic derivative as does the former.

13. Phosphoric acid reacts with edestin as a monobasic acid, in accordance with its dissociation into the ions  $H$  and  $H_2PO_4$ . But little more than the calculated quantity of this acid is required to dissolve a given amount of edestin.

14. Edestin forms a salt with nitric acid, which corresponds to the bichloride. At  $30^\circ$  edestin binitrate is much more soluble in pure water than at  $20^\circ$ , so that a clear solution containing 5 per cent. of this salt yields a considerable precipitate on cooling.

15. Edestin reacts with potassium or sodium hydroxide in a proportion equivalent to that with which it forms the monochloride with hydrochloric acid.

A given quantity of edestin is dissolved by an amount of centinormal potassium or sodium hydroxide solution, which corresponds closely to a proportion of 1 molecule of the base to 1 of protein.

Solutions of potassium and sodium edestin, probably in consequence of hydrolysis, become turbid after standing some time and gradually deposit some of the dissolved protein.

16. About thirteen times as much ammonium hydroxide is required to dissolve a given quantity of edestin as of sodium or potassium hydroxide.

17. About three times as much sodium in the form of carbonate is required to dissolve a given quantity of edestin as of sodium in the form of hydroxide.

18. Edestin conforms strictly with the definition of a globulin, being insoluble in pure water, but readily soluble in neutral solutions of sodium chloride of sufficient strength.

19. Edestin monochloride is, likewise, insoluble in water, but readily soluble in saline solutions. Edestin bichloride and potassium or sodium edestin are soluble in pure water, but insoluble in the presence of a small proportion of a neutral salt. In the presence of a larger proportion of the neutral salt they are soluble, and in such solutions they show the properties of globulin.

20. The fact that edestin, as well as its salts with strong acids, is soluble in perfectly neutral solutions of sodium chloride shows that the solubility of a globulin does not depend on the presence of alkali, as Starke has recently asserted.

[CONTRIBUTION FROM THE BUREAU OF CHEMISTRY, U. S. DEPARTMENT OF AGRICULTURE, No. 42.]

## A STUDY OF THE AVAILABLE MINERAL PLANT FOOD IN SOILS.

BY C. C. MOORE.

Received November 26, 1901.

**I**N a study of soils, it is most essential, to have as wide a variety of types as possible; as at best, the study must be a comparative one. An hypothesis is taken and applied to the maximum number of types, concordant results classified, and the cause of the variations studied. The hypothesis is then amended, after which the work must be repeated according to the revised conditions. If such a study has been systematically carried out, and the variations have been reduced to the limit of error involved in a practical application of the same, then the hypothesis becomes a theory, which is stronger according to the number of types to which it may be successfully subjected.

In the conditions of organic work in nature, there are to be considered, what is the result, and how has that result been obtained? And that these problems are independent, one of the other, is of special significance in the presentation of this paper.

In the formation of a soil, using the word soil, in an agricultural sense, the practical interest is, to what degree of perfection has the work been done? That is, what state of fertility has the soil reached? The fertility of a soil is indicated by vegetation, if climatic conditions can be eliminated. To imitate the results obtained by vegetation, and condense the period of work from months to hours, means to forecast the amount of ingredients which go to make up a crop, which means the opportunity for supplying those ingredients, which would otherwise have been found deficient by the crop. And as such an imitation must necessarily be under purely arbitrary conditions, why should we feel called upon to use a single principle found in nature, other than those which suggest themselves on account of their simplicity.

The simple fact is presented, that a certain species of vegetation has accomplished a definite result, upon a specified type of soil. That the soil has given to the vegetation that amount of mineral matter, which was in a condition to be attacked and assimilated

by the solvent and absorbent properties of the plant. And to estimate the amount of mineral matter which is in such a condition is to forecast the results of vegetation, always barring climatic conditions.

The fact that a crop did take up phosphorus pentoxide to the extent of 20 pounds per acre, is the very best of evidence that at least that much was available for the crop. Just how the crop accomplished the result, and what the long list of chemical reactions are, is at most but of secondary interest.

It is most apparent that the premise in such a line of reasoning is dependent upon the accuracy with which the vegetation indicates the degree of fertility. The growth of a crop is dependent upon the fertility of the soil and climate. In order to study one, the other must be eliminated. The only way to eliminate climatic conditions, is by culture in pots where the moisture and temperature are controlled. By the use of pots, any number of soils may be subjected to the same artificially perfect climatic conditions, which is to eliminate such conditions.

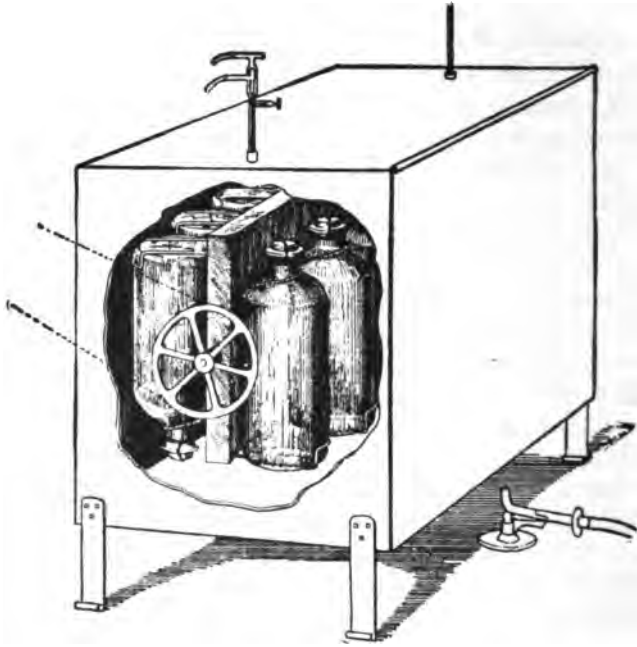
The series of pot experiments, which have been conducted by the department of agriculture for the past five years, has been noticed by most of those in this country, interested in such work. There are 175 pots in use, filled with virgin and cultivated soils and subsoils, including muck soils from Florida. The cropping has consisted of oats and beans, in duplicate pots, thus subjecting each type of soil to cereal and leguminous cropping. Each crop is always followed by buckwheat as a second crop, the same season, the same condition existing every year. A description of the pot culture, together with a detailed description of the methods that have been used in the planting, watering, harvesting, etc., has been prepared by Dr. Wiley, the head of this bureau, and is shortly to appear as the introduction to a bulletin on soil study. Awaiting this, the writer will not make reference to the cropping in detail, and upon which the accuracy of this paper is based.

It is proper to state that the work was originated by Dr. Wiley, who collected the samples with much judgment, and subsequently entrusted the line of research pertaining to the mineral food, and the compilation of such data, to the writer, who, with the exception of the nitrogen determinations, accepts a personal responsibility for the analytical work here presented.

To work backward, is many times the simpler method. If we have unquestionable results which were obtained by a crop, and a sample of the soil which was taken just previous to the planting, we have a definite result for which to work. If it is given what amount of mineral matter must be dissolved from a given amount of soil it is possible to vary the arbitrary conditions, until the desired result is obtained. And the more simple and elastic are the conditions made, with greater ease and accuracy can they be varied. Assuming then that it is simplified to the process of obtaining a definite result by the action of a solvent upon a substance, the conditions of solubility naturally suggest themselves as the solvent and its strength, temperature and time of digestion, degree of agitation and proportion of solvent to substance. In a general sense, to vary any one or more of these conditions is to vary the result. In this study, five hours has been adopted as the time of digestion, it being appropriate to weigh out the samples, digest and filter, in a day's work of seven hours. Two hundred grams of soil per liter are adopted as being comparable with custom and accuracy of solvent effect. The temperature of digestion is fixed at  $40^{\circ}$ , that being the lowest constant temperature obtainable in summer. The question of agitation is of greatest importance, and constant results could be obtained only in the maximum degree, so continuous shaking is adopted. In comparing the effects of shaking by hand, three or four times per hour, with continuous shaking, in the latter case the results were sometimes more than doubled in the potash, other conditions remaining the same. The method employed in this laboratory is that of the slow upsetting device, usually known as the Wagner machine, and making about 40 revolutions per minute. This has the effect of keeping the soil continuously suspended in the liquid. This machine has been modified by Dr. Wiley so as to permit of digestions being made at definite temperatures. The modification comprises a well-fitted double wall sheet iron chamber, in which the revolving shaft together with the attached flasks, are encased. By use of a thermostat, and owing to the circulation of the air as caused by the revolving of the flasks, such a temperature as  $40^{\circ}$  may easily be maintained for hours with no more variation than  $0.5^{\circ}$ .

For a solvent, the simplest mineral acid, hydrochloric, is adopted. The condition admitting of the greatest suscepti-

C. C. MOORE.



bility to variation, is the strength of the acid. Hence, with other conditions fixed, a varying strength giving a corresponding varying solvent action, obtains a series of results, from which the one may be selected that is most concordant with the results that the vegetation is known to have obtained.

For an insight into the general composition of the soils, a complete analysis was made of the mineral substance soluble in hydrochloric acid (sp. gr. 1.115), the digestion being made on a steam-bath, using a reflux condenser, with 10 grams to 100 cc. of solvent. The time of digestion being the all-important question, a series of experiments varying as one, five, ten and twenty hours was made on six varieties of soil. Having no knowledge of the previous presentation of a similar piece of work, the results are here given in Table A.

There is noticed a decided increase in the lime, potash, and soda, which is to be expected, as these result from the decomposition of difficultly soluble silicates, which increase would continue until an absolute digestion had been made. Attention is called to the constancy of the phosphorus pentoxide from one to twenty hours.



TABLE A.

Varying time of digestion for complete analysis.

10 grams soil in 100 cc. HCl of 1.115 sp. gr. Digest on steam-bath.

Series No.	Hours digest.	Insol. residue.	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	Mn <sub>2</sub> O <sub>3</sub>	CaO.	MgO.	SO <sub>2</sub>	P <sub>2</sub> O <sub>5</sub>	NaCl KCl.
13767	1	77.23	6.20	4.98	0.08	0.51	1.25	0.06	0.14	0.71
13767	5	72.50	8.45	5.06	0.13	0.83	1.53	0.08	0.14	0.78
13767	10	72.12	9.15	5.50	0.13	0.90	1.61	0.08	0.15	1.06
13767	20	71.33	9.61	5.54	0.13	1.05	1.61	0.08	0.13	1.21
13768	1	85.53	4.46	3.60	0.08	0.52	1.18	0.04	0.06	0.64
13768	5	....	6.60	3.84	0.08	0.83	1.38	0.04	0.06	0.70
13768	10	81.24	6.50	4.12	0.08	0.97	1.52	0.04	0.06	1.04
13768	20	80.97	6.94	4.14	0.07	1.12	1.53	0.04	0.05	1.12
14094	1	83.43	3.34	3.00	0.08	0.50	0.49	0.07	0.11	0.46
14094	5	80.31	4.37	3.24	0.15	0.62	0.64	0.06	0.11	0.70
14094	10	80.26	5.15	3.32	0.20	0.62	0.68	0.06	0.11	0.97
14094	20	79.55	5.74	3.32	...	0.64	0.67	0.06	0.11	1.13
14095	1	83.72	4.10	3.64	0.08	0.45	0.62	0.04	0.06	0.47
14095	5	80.30	5.84	3.80	0.23	0.55	0.85	0.05	0.07	0.70
14095	10	79.46	6.77	4.16	0.20	0.55	0.85	0.05	0.07	0.92
14095	20	78.13	7.06	4.16	0.20	0.59	0.85	0.04	0.07	1.20
14096	1	77.72	4.14	3.00	0.08	1.30	0.75	0.09	0.18	0.38
14096	5	76.06	5.08	3.08	0.08	1.40	1.03	0.11	0.18	0.70
14096	10	75.14	6.26	3.32	0.10	1.43	1.03	0.11	0.18	0.87
14096	20	74.14	6.52	3.36	0.10	1.46	1.03	0.10	0.18	0.91
14097	1	84.32	4.37	3.44	0.10	0.89	0.90	0.03	0.11	0.47
14097	5	81.65	4.91	3.56	0.21	0.94	1.00	0.04	0.11	0.67
14097	10	81.19	6.36	3.76	0.19	0.98	1.14	0.04	0.11	1.00
14097	20	79.95	6.72	3.80	0.19	1.00	1.13	0.04	0.12	1.21

From a study of this table it was concluded that a digestion of ten hours would give a fairly approximate composition.

In Table B, are given the complete analyses of the soils which are to be considered in this study, together with the average actual yield of each for three successive years, and are graded according to such yield, the conditions of digestion being 10 grams of soil in 100 cc. of hydrochloric acid (sp. gr. 1.115), on a steam-bath, with reflux condenser, for ten hours, shaking every hour.

The determination of total potash and phosphorus pentoxide was also made, the method being to weigh out 2 grams of soil into a 2-inch platinum dish, and ignite over a Bunsen burner to drive off organic matter. Get the soil as much as possible on one side of the dish and put in 1 or 2 cc. of hydrofluoric acid. Allow

the soil to come in contact with the acid very slowly to avoid loss by sputtering, using a platinum stirring rod. After the violent action has ceased, place on a steam-bath and evaporate to dryness. Repeat this operation one or two times and then take up with a little hydrochloric acid and water. Filter and wash into a 100 cc. flask, place the filter and contents into the platinum dish and, after drying over the flame, ignite the paper. There will be a small amount of the coarse mineral, which is transferred to an agate mortar to be ground, after which it is again digested in hydrofluoric acid, until there is no insoluble residue left. Take up in hydrochloric acid and water, and add to the original washings.

The method was found to be very easy and rapid of manipulation, and such a method of solution can not be questioned. It is not seen why efforts are made to use methods involving the use of large amounts of sulphuric acid and mercury, or commonly known as a Kjeldahl digestion, when the use of hydrofluoric acid has been made so simple as it is to-day. The results of the total digestion are tabulated in Table B.

It appeared interesting to know how much of the potash and phosphorus went into solution in the successive stages of digestion, and if it was necessary to obtain a complete solution. This was ascertained by keeping the successive digestions separate for analysis. A soil was ignited to drive off organic matter. Two samples of 5 grams each were taken: one was pestled to a rather fine powder, the other remaining in its natural condition. To each was added about 10 cc. of hydrofluoric acid and run down to dryness, taken up with 0.5 cc. of hydrochloric acid and water. Potash and phosphorus were determined in each, the duplicates agreeing. The residues were again digested, and treated as above, no trace of potash or phosphate being found. The second residue was digested as above until a complete solution was effected, in which no phosphate or potash could be found.

Again 5 grams of the same soil were digested with hydrofluoric acid and run down to dryness, and hydrofluoric acid added a second time, again run down to dryness and taken up with hydrochloric acid. The residue weighed 0.70 gram. This was treated again, the residue weighing 0.25 gram. The next residue weighed 0.15 gram, and the last residue 0.04 gram, or less than 1 per cent. of the original sample. This sample was not ground

TABLE B.  
Digestion in HCl of 1.115 specific gravity for 10 hours on steam-bath.  
Soils arranged in descending magnitude.

Fol.	Insol. Res.	K <sub>2</sub> O.	Na <sub>2</sub> O.	CaO.	MgO.	MnO <sub>2</sub> .	Fe <sub>2</sub> O <sub>3</sub> .	Al <sub>2</sub> O <sub>3</sub> .	P <sub>2</sub> O <sub>5</sub> .	SO <sub>2</sub> .	CO <sub>2</sub> .	Nitric N.	Total N.	C.	H.	Total K <sub>2</sub> O.	Comparative Grade.
76	80.605	0.766	0.178	0.675	0.615	0.059	2.920	5.577	0.138	0.054	0.048	0.0011	0.173	3.38	0.66	2.491	100
77	88.253	0.230	0.047	0.405	0.412	0.072	1.756	3.229	0.135	0.050	0.077	0.000	0.090	4.12	0.41	1.970	98
78	80.553	0.643	0.119	0.575	0.501	0.083	2.880	5.081	0.089	0.042	0.054	0.000	0.174	3.40	0.66	2.418	93
79	84.602	0.273	0.078	0.405	0.550	0.053	3.136	3.878	0.131	0.068	0.102	0.0046	0.147	3.32	0.61	1.570	88
80	87.644	0.296	0.060	0.535	0.457	0.085	2.094	3.113	0.163	0.040	0.073	0.0011	0.105	2.06	0.43	1.510	88
81	80.715	0.731	0.125	0.870	0.907	0.010	3.960	5.455	0.185	0.076	0.052	0.0011	0.146	2.02	0.62	4.356	80
82	79.809	0.525	0.180	0.610	0.643	0.110	3.440	5.590	0.108	0.081	0.070	0.000	0.181	3.27	0.71	1.890	80
83	76.480	0.365	0.125	1.185	0.662	0.083	3.040	5.232	0.093	0.081	0.014	0.0049	0.297	5.51	0.85	0.394	78
84	72.015	0.508	0.115	0.900	1.542	0.050	5.976	9.397	0.117	0.111	0.044	0.0033	0.140	2.72	0.86	1.247	75
85	88.666	0.134	0.039	0.405	0.261	0.032	1.746	2.143	0.066	0.038	0.090	0.009	0.096	5.68	0.40	1.585	75
86	80.479	0.118	0.043	0.490	0.275	0.037	1.631	1.702	0.064	0.041	0.080	0.0011	0.126	2.72	0.66	2.156	65
87	84.195	0.390	0.098	0.685	0.628	0.030	2.720	3.817	0.153	0.107	0.070	0.0017	0.185	2.72	0.65	1.974	64
88	80.760	0.496	0.116	0.465	0.450	0.045	3.260	5.254	0.185	0.069	0.021	0.0017	0.213	3.42	0.95	1.402	64
89	74.604	0.479	0.127	1.455	0.989	0.071	1.472	6.248	0.185	0.109	0.068	0.000	0.301	4.95	0.95	1.402	57
90	88.200	0.161	0.063	0.210	0.247	0.015	1.872	3.913	0.066	0.053	0.037	0.000	0.074	1.85	0.52	1.359	57
91	85.545	0.321	0.047	0.250	0.518	0.070	3.000	3.536	0.186	0.045	0.054	0.0017	0.122	2.81	0.51	1.753	51
92	81.555	0.153	0.122	0.525	0.558	0.015	3.886	4.476	0.144	0.063	0.053	0.0011	0.114	2.76	0.52	1.327	51
93	88.620	0.351	0.122	0.140	0.585	0.040	3.320	4.057	0.156	0.046	0.059	0.0022	0.073	0.86	0.37	1.867	51
94	86.305	0.365	0.071	0.710	0.585	0.040	3.360	2.923	0.147	0.085	0.068	0.0024	0.168	3.18	0.62	1.820	51
95	81.920	0.337	0.116	0.790	0.595	0.040	3.120	4.618	0.137	0.044	0.024	0.0017	0.045	0.82	0.28	1.815	48
96	74.337	0.594	0.086	1.535	1.726	0.020	5.640	7.697	0.163	0.068	0.048	0.0011	0.095	1.58	0.38	1.494	48
97	90.659	0.156	0.053	0.230	0.218	0.020	1.476	2.945	0.070	0.043	0.010	0.0024	0.158	2.59	0.60	1.494	48
98	81.970	0.384	0.114	0.370	0.450	0.040	3.400	5.370	0.105	0.047	0.010	0.0024	0.158	2.59	0.60	1.856	48
99	80.570	0.747	0.132	0.970	1.105	0.040	4.260	6.119	0.176	0.073	0.071	0.0024	0.080	1.69	0.54	1.278	48
100	85.198	0.204	0.077	1.012	0.299	0.088	2.727	5.123	0.168	0.044	0.071	0.0024	0.096	1.60	0.50	1.905	48
101	77.686	0.480	0.283	1.415	1.661	0.085	5.280	7.103	0.147	0.098	0.016	0.0046	0.068	1.01	0.25	1.905	45
102	97.500	0.554	0.053	0.050	1.054	0.005	8.800	1.840	0.035	0.022	0.100	0.0046	0.169	2.48	0.69	1.708	45
103	77.300	0.246	0.111	0.125	0.549	0.040	6.200	6.920	0.230	0.066	0.066	0.0028	0.105	2.08	0.44	1.805	38
104	86.750	0.733	0.127	0.525	0.687	0.040	3.640	1.615	0.202	0.066	0.030	0.0024	0.111	2.05	0.61	2.592	33
105	79.813	0.733	0.127	0.525	1.005	0.130	4.840	6.372	0.090	0.068	0.030	0.0024	0.106	0.82	0.31	1.907	33
106	91.221	0.193	0.061	0.157	0.248	0.040	1.623	3.412	0.051	0.018	0.024	0.0017	0.046	0.82	0.31	1.907	27
107	79.604	0.580	0.167	0.520	0.886	0.065	4.200	6.935	0.085	0.053	0.051	0.000	0.093	1.84	0.67	1.565	19

previous to digestion, and the residue was probably some coarse matter that was decomposing slowly.

Then a series of samples were digested as above, hydrofluoric acid being added the second time before taking up in hydrochloric acid. All the residues were put together and brought into complete solution. No phosphate or potash was found, which is good evidence that not even a complete digestion is essential.

The mechanical composition of the soils also, is illustrated in Table C.

TABLE C.  
Arranged in descending magnitude. Mechanical composition of the soils.  
Per cent.

Pot.	mm. >0.25.	mm. >0.10.	mm. >0.05.	mm. >0.025.	mm. >0.012.	mm. >0.006.	Will not float 18 hrs.	Will float 18 hrs.	Loss on ignition.
76	1	4	28	32	7	3	8	8	8
27	4	10	12	25	16	9	10	7	5
7	2	4	26	35	7	3	7	9	9
16	2	4	16	37	9	5	11	9	7
90	2	4	12	27	20	9	11	7	5
18	2	5	31	20	15	4	6	9	7
5	..	..	..	..	..	..	..	..	..
74	13	23	11	14	12	3	4	7	12
65	1	13	8	15	8	4	18	13	9
80	12	36	21	7	8	4	2	2	5
14	20	37	15	7	7	3	2	1	6
22	14	30	16	14	9	3	2	5	7
9	3	4	9	26	11	9	18	9	9
70	2	6	7	25	10	6	15	15	2
3	2	14	17	34	11	6	12	8	2
25	1	32	33	11	10	3	2	5	3
19	21	20	15	15	9	3	8	1	7
12	3	9	52	20	3	2	2	2	6
51	21	24	15	13	6	3	10	5	2
87	14	21	22	11	8	2	1	4	6
39	14	20	16	16	6	4	8	7	8
63	6	14	20	11	15	5	8	14	7
69	2	5	12	34	19	9	8	7	4
73	6	5	9	22	27	6	8	7	7
84	1	2	30	20	16	4	8	12	6
29	11	15	11	19	8	7	15	9	6
31	7	20	24	11	10	5	7	11	5
89	1	27	42	8	7	5	3	5	2
1	10	17	18	12	12	5	8	11	8
85	18	23	16	13	6	3	9	5	5
104	1	2	19	32	7	4	12	16	7
93	10	17	19	11	12	5	8	10	8
101	2	5	12	33	20	8	7	9	3

In this, a method was to some extent improvised, it being in the main the beaker decantation, or what is more generally known as the Osborne method. The radical change was a method devised for the disintegration of the sample. Instead of pestling with a rubber-tipped pestle, the sample was agitated in water by means of a shaking machine. Twenty grams of soil were put into a cylindrical bottle, the ordinary 8 oz. sterilizing bottle being used, with about 150 cc. of water, and the bottle shaken about one hour at the rate of 150 strokes per minute. A frame was constructed to hold ten or more such bottles. The method proved admirable in every respect. Samples shaken one hour and one week gave constant results, disproving any grinding of particles. The siftings were made through sieves and bolting-cloth, the decantations controlled by the microscope. Below 0.006 mm., the decantation could be made with no accuracy, and resort was had to an arbitrary floating method. The period of eighteen hours was selected, as it was convenient to arrange for the settling at the close of a day's work, and to decant the next morning. This decantation or what is specified as "does float eighteen hours," was determined by difference.

While this separation of particles below 0.006 mm. is altogether arbitrary, it is no more so than the practice of endeavoring to measure with the microscope, and decant particles below that size, the inaccuracy of measurement being so great. In this work, the writer found it very convenient to make the coarser separations in the working hours, and at the close of each day, to stir the sediment and allow to stand until it could be decanted next morning, the time being about eighteen hours. It took five or six days to complete the separations, and that many decantations of eighteen hours' standing gave a clear decantation at the last, after which the residue was weighed to represent that portion that was below 0.006 but would not remain in suspension eighteen hours.

As this paper will relate to the oat plant, only data for such pots will be presented. In most instances the subsoils failed to make what could be called crops, so these and the muck soils, being abnormal conditions, were not considered, except in a few instances, while again, some of the so-called subsoils were practically soils, the subsoil being the second six inches. In some other cases there was insufficient sample to admit of the work,

so the data given is not a selection, but comprises all soils which produced crops, and of which there was sufficient sample for study.

The crop data for the five years since the first planting, is illustrated in Table D.

The weight of soil in the pots varies from 23 to 30 kilos. The crop weights are expressed in parts per 100,000 of the soil, while the ash, nitrogen, potash and phosphorus pentoxide are expressed in parts per 1,000,000 of the soil. This method of expression makes the results comparable. It is observed there are two columns under each of the headings. In all cases, the left column refers to the first crop, oats, and the right column, to the second crop of that season, buckwheat. For illustration, pot 1 contains 31.1 kilos of soil. It was not planted until 1896, when the weight of the oats in parts per 100,000 is expressed as 159, and the following buckwheat crop as 105. The crude ash of the oats is expressed in parts per 1,000,000 of the weight of the soil as 197, and of the following crop of buckwheat as 124. The nitrogen is: oats 18 parts per 1,000,000, and buckwheat 13; potash in oats as 60, in buckwheat as 36, and phosphorus pentoxide in oats as 16, and buckwheat 12. Continuing horizontally, the crops and their respective analyses are expressed for each subsequent year in a similar manner.

In pot 3, it is seen that there was a crop of oats raised in 1895, but no second crop of buckwheat, while thereafter the two crops were raised annually.

In an average crop of oats of 45 bushels per acre, if the weight of total crop be computed on the area of a circle 12 inches in diameter, which is the area of the pot, and that weight compared with the average weight of soil in the pots, and expressed in parts per 100,000, the ratio will be 100; that is to say, under the column headed "crops," the normal crop will be expressed by 100.

It is noticed that many of these crops are very much above the normal. But when it is considered that the moisture and temperature, have been ideal, and that some of the soils are of our richest virgin types, it is anticipated that the crop will utilize all assimilable food, provided there is an approximate balance of the essential elements; that is to say, a soil with a superabundance of potash, and a decided deficiency of phosphate, is not ex-



pected to furnish to the crop all of its available potash, or as much as it would were the deficiency in phosphate made up. Further, it is rational to expect that, with a soil abounding in one element, as potash for example, and deficient in another, as phosphate, the crop would feed more greedily on the deficient element, in its effort to make a balance in its composition. In other words, a crop feeding on a soil highly supplied with one element, and deficient in another, would take from the soil more of the deficient element than would be considered available under normal conditions.

In a study of Table D, it is seen that the columns headed  $K_2O$ , and  $P_2O_5$ , are very indicative. There is shown here the actual amounts that the crop obtained under ideal conditions of climate. Can not the ratios 60 and 16, as shown in pot 1, be interpreted as representing the available amounts of potash and phosphate, which the soil held ready for that crop at the time of planting, assuming of course the possibility that one of these elements may be largely in excess of that required for a balanced composition? There is no other standard for what a soil should do, than what it actually does under ideal climatic conditions.

It is readily conceived that while the mineral matter in a soil is not soluble in water, still some of it may exist in such a degree as to become soluble in the acids in the sap of roots. If we know how much the root acid was able to dissolve, can not any simple acid be diluted until it will accomplish the same result? Accordingly, the results sought are those under the headings  $K_2O$ , and  $P_2O_5$ , in the left column as representing the available potash and phosphate respectively.

The simplest acid, hydrochloric, and the solvent conditions as previously referred to, are taken with the purpose of diluting the acid, until its solvent effect reaches a point where it is comparable with the actual conditions.

A preliminary digestion is made to determine the basicity of the soil, and a correction made in the strength of the acid so as to reduce the solvent action to a uniform basis. It is understood that where a digestion is spoken of as being made in  $N/50$ , for illustration, that the solvent was stronger than  $N/50$ , but after digestion, the filtrate was  $N/50$ . For example, 20 grams of soil were digested in 100 cc. of  $N/10$  hydrochloric acid for five hours at  $40^\circ$ , constant shaking, and 10 cc. of filtrate titrated with  $N/1c$



alkali, using methyl orange as an indicator to avoid carbon dioxide. Suppose 9 cc. of alkali are required to neutralize. Then 1 cc. of acid was neutralized by the basic matter, and consequently 1 cc. additional of the  $N/10$  acid must be allowed for, or 10 cc. of an unknown strength must be the equivalent of 11 cc. of  $N/10$ . Therefore, 10 cc.  $N/X$  must equal 11 cc.  $N/10$ , or  $X$  equals 9; that is, the solvent should be  $N/9$  in order to have a filtrate  $N/10$ .

While it is not exactly theory, it is within the limit of error that a solvent of strength of  $N/90$  on such a soil gives a filtrate of  $N/100$ . In like manner,  $N/180$  gives a filtrate of  $N/200$ .

A series of results were obtained in  $N/10$  hydrochloric acid. They ranged from two to seven times the results as shown in the crops. A second series in  $N/25$  acid, other conditions remaining the same, gave in some soils about half that obtained in the  $N/10$ , while in others nearly the same. In the same manner, the strength of the acid was successively divided until the dilution corresponded to  $N/200$ . The results are tabulated in Table E.

In Table F, a comparison is made between the results obtained by the crop, and those obtained by a digestion in  $N/200$  hydrochloric acid, the soil sample being taken before planting.

The two columns on the left are expressed in parts per 1,000,000 of the soil, soluble in  $N/200$  hydrochloric acid, and the two columns on the right are parts per 1,000,000 of the soil taken up by the crop, these results being taken from Table D. The results are most striking. In pot 1, the ratios of 16 and 65 against 16 and 60 are singularly coincident, and represent a soil well balanced in plant food. In the following year, there was but half the amount of phosphate available, and apparently more potash. Pot 3 shows a soil most deficient in phosphate and abundant in potash. It is reasonable to suppose that on such soils, a crop would be ravenous for phosphate and so feed on phosphate that would not be considered available under normal conditions, while at the same time it would not utilize all of its available potash. This is the best illustration of a soil unbalanced in plant food. By reference to Table D, it will be seen that the soil shows its poverty throughout. Pots 5, 7, and 9 are also poorly balanced. Pot 12 is decidedly an inferior soil in mineral food. While the acid-soluble potash is coincident with the crop result, it would not be expected that the crop would obtain comparatively so much phosphate. However, it is ex-

TABLE E.  
Successive Digestions in Acids of Different Strengths.

P <sub>2</sub> O <sub>5</sub> .							K <sub>2</sub> O.							
Per cent.			Parts per million.					Per cent.		Parts per million.				
Pot.	Total.	strong HCl.	N 10	N 25	N 50	N 100	N 200	Total.	strong HCl.	N 10	N 25	N 50	N 100	N 200
E	0.384	0.230		105	63	35	16	1.768	0.554					65
1*							8							84
3	0.102	0.066			2	2	2	1.350	0.161			144	129	102
3*					4	4	2						116	92
5		0.106		6	6	5	5		0.525			191	153	105
7	0.147	0.089			15	10	7	2.418	0.643			223	166	144
7*						9	7						133	101
9	0.192	0.166					5	1.974	0.496					77
12	0.409	0.144			6	2	1	1.527	0.153				104	
12*							1							27
14	0.096	0.062	41	24	13	13	9	1.585	0.118	184	182			45
14†					8	7	4					57	55	31
16*	0.134	0.121					2	1.570	0.272					40
16†					70		1					131		41
18	0.275	0.185		280	114	24	10	4.356	0.731		425	310	235	175
19	0.281	0.189		48	27	20	18	1.751	0.321			405	317	235
19†					21	13	12					230	173	134
20					5	5	5					44	30	28
22	0.179	0.153		50	20	5	4	2.156	0.390				147	66
25	0.083	0.032		16	15	15	11	1.062	0.093		76	74	58	47
25*					8	8	8					61	44	37
25†					6	4	3					56	48	38
27	0.162	0.125	128	60		18	16	1.970	0.230	127	107	80	64	60
27†														54
29	0.172	0.168	37	13	4	1	1	1.278	0.204	135	98	94	86	80
29*						1	1						70	58
29†					3	1	1					82	66	63
31	0.281	0.147				34	16	1.905	0.480				24	20
31†							18							69
35		0.083	2	2	1	1	1		0.580	168	168	115	69	69
39*	0.160	0.137				5	4	1.829	0.337				28	20
51	0.243	0.153			30	13	3	1.867	0.351			99	90	76
63	0.339	0.163		122	112	57	25	1.815	0.594		225	159	110	84
63*					91	33	21					160	105	71
65		0.117					2		0.508					50
69*	0.070	0.070					1	1.494	0.156					47
70	0.275	0.185					14	1.402	0.479					24
73	0.160	0.105		2	2	2	1	1.856	0.384				67	27
74*	0.294	0.093					20	1.890	0.365					30
76	0.192	0.128		57	42	42	33	2.491	0.766		920	705	560	525
76*							31							402
76†					25	23	13					626	452	366
80	0.102	0.066			10	6	5	1.247	0.134			171	171	170
80*							4							67
84		0.176					9		0.747					88
85	0.313	0.205		44	44	17	10	1.805	0.246			283	238	171
86				74	40	26	25				377	191	148	118

\* Second year.

† Third year.

TABLE E.—Continued.

P <sub>2</sub> O <sub>5</sub> .							K <sub>2</sub> O.													
Per cent.			Parts per million.				Per cent.		Parts per million.											
Pot.	Total.	Strong HCl.	N 10	N 25	N 50	N 100	N 200	Total. o	Strong HCl.	N 10	N 25	N 50	N 100	N 200						
87	0.166	0.147	28	44	25	5	2	2.190	0.365			72	50	45						
89	0.089	0.035		22	19	13	13	1.095	0.053			103	88	74						
89*							11							61						
90	0.262	0.163		104	68	68	68	1.510	0.295			103	74	58						
90*					62	55	42					95	74	46						
90†				44	44	27			88	72	58									
93	0.300	0.233	101	64	57	25	1.907	0.509				93	88	46						
93*				60	16	5				178	78	66								
101	0.083	0.051	15	10	2	1	1.565	0.193	361		280	159	166							
104	0.147	0.090					2.592	0.733						233	171	147				
104†							2	1						1						
115														1						16
117															3					12
156						1							27							
158							5							27						
160					1	1	1					28	28	22						
162							4							147						
164					4	2	2					27	25	17						
166					1	1	1					199	180	160						
168					15	10	6					209	156	127						
170							1							35						

\* Second year.

† Third year.

pected that the crop would feed ravenously for phosphate, and so take up more than is apparently available. Pot 18 is another illustration of superabundant potash. By referring to Table E, it will be seen that in N/100 acid there is two and a half times as much phosphate soluble as in N/200; that is to say, there is much phosphate just beyond the line of that interpreted as being available, so it could be foretold that with so much available potash, more phosphate would be assimilated. Pot 19 is in striking contrast. Here is a great excess of potash shown to be available, but, as seen in Table E, there is but one-ninth more soluble in double the strength acid. Consequently, this soil would not be expected to supply much more phosphate than that interpreted as available, even though the potash is most abundant. In pots 20 and 22, the interpreted plant food is nearly coincident with the actual conditions. In pot 25, the food elements are poorly balanced, the potash figures agreeing very well and showing a deficiency in phosphate. Pot 29 seems totally lacking in available phosphate, and well supplied in potash. Pots 31 to 51 are virgin subsoils. It is interesting to note the change in the

TABLE F.

Comparison of mineral matter soluble in  $N_{100}$  HCl, with that taken off by crop.  
[Parts per million.]

Pot.	Proposed available.		Taken off by crop.		Type.	Pot.	Proposed available.		Taken off by crop.		Type.
	P <sub>2</sub> O <sub>5</sub>	K <sub>2</sub> O.	P <sub>2</sub> O <sub>5</sub>	K <sub>2</sub> O.			P <sub>2</sub> O <sub>5</sub>	K <sub>2</sub> O.	P <sub>2</sub> O <sub>5</sub>	K <sub>2</sub> O.	
1	16	65	16	60	Vir. sur.	65	2	50	5	66	Cul. sur.
1 <sup>1</sup>	8	84	10	36	"	69	1	47	4	37	"
3	2	102	4	42	"	70	14	24	12	46	"
3 <sup>1</sup>	2	92	5	43	"	73	1	15	5	18	"
5	5	87	8	79	"	74	20	30	11	49	"
7	7	144	8	98	"	76	31	402	29	98	"
7 <sup>1</sup>	7	101	7	55	"	76 <sup>1</sup>	13	366	16	92	"
9	5	77	5	42	"	80	5	170	6	41	"
12	1	27	7	26	"	80 <sup>1</sup>	4	67	10	53	"
14	9	45	7	40	"	84	9	88	12	46	"
14 <sup>1</sup>	4	31	4	20	"	85	10	171	11	34	"
16	2	40	4	44	"	86	25	116	27	99	"
16 <sup>1</sup>	1	41	4	37	"	87	2	45	5	46	"
18	10	175	15	82	"	89	11	61	4	31	"
19	18	235	17	76	"	90	68	58	25	71	"
19 <sup>1</sup>	12	134	12	..	"	90 <sup>1</sup>	42	46	20	39	"
20	5	28	..	24	"	90 <sup>2</sup>	27	58	25	31	"
22	4	66	5	58	"	93	25	46	6	37	"
25	11	47	5	41	"	93 <sup>1</sup>	5	34	5	7	"
25 <sup>1</sup>	8	37	4	29	"	101	1	31	4	31	Cul. sub.
25 <sup>2</sup>	3	38	3	20	"	104	1	166	5	45	"
27	18	60	21	77	"	104 <sup>1</sup>	1	147	3	19	"
27 <sup>1</sup>	16	54	13	..	"	115	1	16	1	11	"
29	1	80	6	35	"	117	3	12	2	10	"
29 <sup>1</sup>	1	58	6	15	"	156	1	27	3	21	W108
29 <sup>2</sup>	1	63	5	17	"	158	5	27	10	30	W11
31	16	20	16	41	Vir. sub.	160	1	22	4	24	B1A
31 <sup>2</sup>	18	69	14	(24)	"	162	4	147	15	76	W13
35	1	69	1	18	"	164	2	17	13	29	B2A
39	4	20	6	33	"	166	1	160	6	54	B3A
51	3	76	10	65	"	168	6	127	16	64	B4A
63	25	84	14	62	Cul. sur.	170	1	35	4	30	W3
63 <sup>1</sup>	21	71	15	21	"						

<sup>1</sup> Second year.

<sup>2</sup> Third year.

soil in 31 after one year, the potash increasing from 20 to 69. This is the subsoil of pot 1, and it will be noticed that the phosphate is the same, while in the second year the potash is the same. The soil and subsoil are practically the same, as will be seen in the mechanical analyses. In pot 51 it will be noticed that the crop fed more on phosphates than shown in the analysis. By Table E,

it will be seen that the phosphate went from 3 to 13 in the next strength acid, showing that more phosphate was very nearly available, and which became so after the subsoil had been exposed to the air.

This concludes the virgin soils that were studied. Pots 63 to 90 inclusive, are cultivated soils. Pot 63 is overbalanced in phosphate. It would be expected that more than 84 parts of potash would be utilized, rather than only 62. This crop as seen in Table D, is impoverished in nitrogen. It is more probably suffering for want of a better crop rotation system. It will be noticed that the crop is two and a half times greater the first year than in the second. Pots 65 to 74 are similar to soils, to which reference has been made. Pot 76 is extraordinarily fertile, so far as the immediately available phosphate is concerned. But in Table E, it is noticed that in N/100 acid, about one-fourth more is soluble than in N/200, while N/50 gives no increase over N/100. In this soil, the first crops would be expected to abound in phosphate, followed by a rapid deterioration in that element. This is noticeable in the following year, where the phosphate falls to 13, and throughout the crop records of that soil. Pot 85 is fairly well supplied in phosphate and potash, but the crop is only 76, or about three-fourths a normal crop, so the soil is suffering for some other essential element, or more probably from improper crop rotation. Pot 86 is the best type of a soil balanced in these plant foods, its crop being about two and a half times the normal.

The ratio of 25 parts of phosphate to 100 parts of potash, seems to be the ideal condition. This ratio of 1 to 4 seems to exist in most of the soils.

In pot 89 there is a discrepancy not understood when the phosphate and potash only are considered. Pot 90 contains more than double the amount of available phosphate that is found in any other soil, but its deficiency in potash is foreseen. The waver in the potash as seen in the three years in which this soil was studied, is proportional to the waver shown in the cropping, the first and third years being constant, with the drop in the middle.

Pots 93 to 117 are subsoils upon which the same diagnosis seems to hold. Subsoils are an abnormal condition, and so few of them produced a crop that not much can be seen from the small data here presented.

Pots 156 to 170 are soils taken from the famous wheat and

barley fields of Rothamsted, England. As is well-known, these fields have been under continuous study for more than half a century. The plot references as given in the Rothamsted memoranda, are shown in the column headed W10a. Some of these plots have been treated with excessive quantities of artificial plant food, as ammonia salts, sulphates of potash, soda, and magnesia, and superphosphate of lime, so that the condition is most abnormal in cases where all of these compounds have been applied to a single plot. In pots 156, 160, and 170, only nitrogen has been applied. In these pots the interpreted potash is nearly coincident with the crop record, and the phosphate is shown to be as deficient in the crops as would have been anticipated from the soil analysis. Pot 158 has had continuous application of superphosphate. This is shown in the analysis but not to the extent taken up in the crop. It is well-known that the available phosphate in a superphosphate is constantly reverting to an insoluble form, and it is rational to suppose that, as this sample of soil was on hand for over three years before the analysis was made, in that time some would have reverted that would have been soluble, had the analysis been made at the time the crop was planted. However, the potash is seen to be practically coincident. In pot 162, superphosphate and potash had been added. The increase of available potash is shown in the analysis and in the crop, it not being expected that the total available would be utilized, as has been pointed out in previous cases of a superabundance of one element. The increase in the phosphate is shown, but not to the extent indicated by the crop for the reasons as cited in reference to pot 158. All of the soils have been studied nearly four years after the sample was taken. In pot 164, only superphosphate has been added. As this soil is similar to pot 158 in the matter of potash, it is more than probable that the result 17 is low, due to an analytical error. By a reference to Table E, it is seen that these soils are nearly identical in potash in the N/100 and N/50 digestions. Pot 166 has been treated with potash as is shown in the analysis, but deficient in phosphate, while pot 168 has received both potash and phosphate, as is shown in the analysis. The same condition in the matter of phosphate exists, as was referred to in pot 158.

Now to look at this Table F, as a whole, there are about 65 pots studied, covering a range of soil types from Massachusetts

to California. The soils have been taken with the one purpose of having as much variation as possible. It is not a selection of evidence that is comparable, but is all the material that was available for study. With the exception of about two instances, the analyses indicate, to a remarkable degree of accuracy, the conditions as brought out in the crops. Just how much circumstantial evidence is necessary to establish a fact, is always questionable, and whether the data here given is sufficient proof, is not the province of any one man to decide, as to its being a means for forecasting the mineral plant food available for an oat crop.

The simplicity and rapidity of the method will undoubtedly appeal to any one. All chemists have noticed the degree to which analytical methods may be simplified by actual experience. In this method the ratio of substance to solvent was 200 grams per liter. However, a liter flask was used in which 186 grams of soil were placed, and the solvent added up to the mark. This varied only 1 or 2 cc. from 930, which was the ratio desired. After the digestion the whole was shaken and emptied on to a fluted filter sufficiently large. After draining, the volume of the filtrate did not vary 10 cc. from 800. This was shown in so many cases, that the filtrate was no longer measured, but taken as 800 cc., corresponding to 160 grams of the soil. This expedited the work greatly, and avoided the recording of figures, and the chance for mistake. To this filtrate was always added 1 or 2 cc. of nitric acid for the double purpose, of decomposing any ammonium chloride which may have been formed in the digestion of organic matter, and also to oxidize any organic matter in solution. After evaporating to dryness, hydrochloric acid was added repeatedly and evaporated until there was no further evidence of the presence of nitrates. The residue was now transferred to a smaller porcelain dish, and diluted to about 50 cc. with water. To this was added 2 cc. of platinum chloride, according to the method of direct estimation of potash as found in this Journal, 20, 340 (1898). The solution was slowly concentrated until the potassium platinichloride could be crystallized on the sides of the dish, after which it was set off to cool and solidify. It was then treated with acidified alcohol as described in the method referred to, washed onto a paper filter, and washed with plain alcohol and then with the half-saturated solution of ammonium chloride, according to the usual method. After drying

the salt, it was dissolved and washed through with hot water into small platinum dishes, evaporated to dryness, dried at  $100^{\circ}$ , and weighed. The filtrates were set aside after the washing with ammonium chloride, stirred up and the ammonium platinum chloride allowed to settle over night. Most of the liquid can then be decanted into porcelain evaporators. The residue is washed onto a filter with alcohol three or four times, the washings being added to the original solution for evaporation. A rather large dish should be used and the evaporation carried on slowly, until the alcohol is completely volatilized. There is left a large residue of ammonium chloride, which should be well diluted with water, and 2 or 3 cc. of nitric acid are added. The dish should be covered at first and warmed very gently to avoid loss by spirting. After the salt has been decomposed, the evaporation may be completed. The residue is taken up with water and a few drops of nitric acid, and the determination of phosphorus pentoxide made according to the usual molybdate method, titrating the yellow precipitate. It is seen that the results in potash and phosphorus pentoxide are to be calculated on the original 160 grams of soil, which is a great advantage in accuracy over dividing the original solution.

As to the accuracy with which these results can be obtained, the writer has found no more variations in duplicates, where the results are expressed in parts per million than in analytical determinations where the results are expressed in parts per hundred. Several sets of samples were repeated through mistake, the results being practically the same in all cases, and in some, identical.

By following such a procedure, the writer has found it very easy to make such analyses, averaging ten samples per day of seven hours' work, where the evaporations could continue through the night. Samples could be completed within four days. The daily expenditure, including salary of the analyst, chemicals, portion of house rent and the help of porter in the preparation of samples, is less than \$5 at this laboratory. This means that samples could be brought to such a laboratory, and four days later the results could be received as to the immediately available phosphate and potash, at a cost less than 50 cents per sample.

A method of soil analysis to be valuable, must be cheap and rapid. It is not enough to say that a soil is deficient in phosphate for example. It should be ascertained how deficient. If



a soil analysis shows 10 parts per 1,000,000 of phosphorus pent-oxide, and the intended crop requires 20, it is more reasonable to add the deficient 10 parts than to pronounce the soil deficient in phosphate and proceed to add the 20 parts which the crop will need. If a soil is totally deficient in every plant food, it is generally known that such a soil cannot be fertilized with profit. It is only where there is a partial deficiency, or a poorly balanced soil, that the use of artificial food is economy. In a true sense of economy, the agriculturist should know from the analysis supplied him, as to whether a full or partial fertilization is profitable. Suppose he finds his potash to be somewhat below the normal requirement, and his phosphate to be about half deficient. Will he supply the phosphate until it balances the potash, or will he increase the potash up to the normal, and balance the phosphate with that. In the first case it would be the equivalent of buying something in order to make something that he has, profitable, while in the second case he would be buying something which required the purchase of something else, in order to make either profitable.

In the study of the Rothamsted soils, the opportunity is offered to compare results obtained by the method as above proposed, and that published by Dyer in the *Journal of the Chemical Society*, 1894, upon the use of 1 per cent. citric acid as a solvent for available plant food. There are but four of the soils which were studied by Dyer, namely, pots 160, 164, 166, 168. His samples were taken to the same depth as those sent to the Department of Agriculture. The results are expressed in parts per 1,000,000 and compared with those obtained by the hydrochloric acid and the crops.

TABLE G.

Comparing one per cent. citric with N/200 hydrochloric acid.  
[Parts per million.]

Pot.	Supposed available.		Taken off by crops.		Solvent.
	P <sub>2</sub> O <sub>5</sub> .	K <sub>2</sub> O.	P <sub>2</sub> O <sub>5</sub> .	K <sub>2</sub> O.	
160	1	22	4	24	HCl
160	60	20	..	..	citric
164	2	17	13	29	HCl
164	425	23	..	..	citric
166	1	160	6	30	HCl
166	81	407	..	..	citric
168	6	127	16	64	HCl
168	500	300	..	..	citric

In pot 160, a soil that is known to be impoverished in all plant food, the citric acid gives 60 parts per 1,000,000 as representing the available phosphate, an equivalent of 150 pounds per acre, figured to a depth of twelve inches, or as much as good crops of oats would take off in ten years. And in pot 166, another soil known to be totally deficient in available phosphate, the citric acid method shows 81 parts per 1,000,000, an equivalent of 205 pounds per acre, or enough for fifteen years. In the plots that have been fertilized with phosphate, pot 164 would be considered to have 425 parts or 1073 pounds per acre, and pot 168, 500 parts or 1264 pounds per acre, or the equivalent of a good crop feeding for seventy-five years. The total phosphorus pentoxide as obtained by Dyer on the unfertilized soil in pot 160, was equivalent to 2400 pounds per acre, while that on the fertilized soil of pot 168 was 4600 pounds per acre, these two plots being the same original soil. Here is an accumulation of over 2000 pounds of phosphorus pentoxide, of which very little can be available, it having reverted to an insoluble form. However, the citric acid is able to obtain 1200 pounds of this accumulation.

As has been previously referred to, these soils, where they have been fertilized, are so artificial that not much can be learned from a chemical study of them, pot 160 being the only unfertilized soil. In this pot the indications for the potash are very close, and agree with the crop data while in the phosphate there is a wide discrepancy.

It is recognized that this citric acid digestion was the first step toward using weaker solvents, and that the work was done seven years since. And to quote that writer's language, "since the choice of a solvent for use in soil analyses must in the end be empirical, both as regards its form and its strength," it is surprising that the tendency has been to work with citric acid, or acetic, oxalic, aspartic, or any complicated solvent of such a nature. Only last year the investigator of that same work on citric acid, addressed our Association of Agricultural Chemists and very aptly remarked that he saw no reason why its use should be discontinued, as nothing better had been suggested.

It is interesting to notice some of the conditions of solubility as used by Dr. Dyer, as well as many of the American chemists, on this line of work. According to Dr. Dyer's article, "the temperature ranged between 10° and 19° C.," the work being done

in the winter season. The same line of investigation has been continued in this country in summer at "room temperature," which is oftentimes  $30^{\circ}$  to  $35^{\circ}$  C. Here is a range of  $9^{\circ}$  in the digestion as carried on by Dr. Dyer, and an extreme range of  $25^{\circ}$  in the continuation of the work. It may here be worth while to refer to some unpublished results obtained by Dr. W. G. Brown and myself, in reference to the controlling conditions of solubility in citric acid. The results are tabulated in Table H.

TABLE H.  
Soil 29. 200 grams in citric acid.

Liters solvent.	Strength acid. Per cent.	Temp. digest. Degrees.	Time digest. Hours.	P <sub>2</sub> O <sub>5</sub> . Per cent.	K <sub>2</sub> O. Per cent.
1	1	30	5	0.011	0.007
2	1	30	5	0.012	0.008
3	1	30	5	0.014	0.008
1	2	30	5	0.012	0.007
2	2	30	5	0.013	0.007
3	2	30	5	0.013	0.008
1	1	40	5	0.022	0.008
2	1	40	5	0.022	0.008
3	1	40	5	0.026	0.009
1	2	40	5	0.024	0.008
2	2	40	5	0.022	0.008
3	2	40	5	0.030	0.008

It is seen that in variations of 1 to 3 liters of solvent and 1 to 2 per cent. of acid, at a constant temperature of  $30^{\circ}$  C., the phosphorus pentoxide is constant at about 0.012 per cent. and the potash constant at 0.008 per cent. With the same conditions maintained, and the temperature increased by  $10^{\circ}$ , the phosphorus pentoxide is constant at about 0.024 per cent., and the potash remains 0.008 per cent.; that is to say, an elevation of  $10^{\circ}$  in temperature, doubles the solubility of the phosphate. An elaborate piece of research was undertaken to arrive at the strength of 1 per cent. which can at least be doubled without effect, while the extremely sensitive point, the temperature, was not considered. The potash conditions are different. It remains constant at 0.008 per cent., which exactly coincides with the result obtained with N/200 hydrochloric acid (see pot 29, Table F). Also in the unfertilized plots of the Rothamsted soils, in pot 160, Dr. Dyer obtained 20 parts per 1,000,000 against 22 by the hydrochloric acid, and in pot 164, 23 parts against 17, while in the

fertilized plots, as pot 166 and 168, there were 400 parts against 160 and 300 against 127.

It is not intended that these references should undervalue the splendid work done by Dr. Dyer, but will suggest that the time has long since arrived for a second step to be taken in a line of work of importance, incomparable with anything else in scientific agriculture.

For the sake of comparison, the writer has selected a set of ten samples and subjected them to the several methods proposed for the determination of available phosphorus pentoxide and potash. The results are tabulated in Table I. They are arranged in the order of the agricultural value of the soils, as shown by the pot experiments, beginning with the better soil. The results are expressed as parts per 1,000,000.

TABLE I.  
Comparison of proposed methods for available plant food.  
[Parts per million.]

P <sub>2</sub> O <sub>5</sub> .						K <sub>2</sub> O.						
Pot.	N/5 HCl.	Ammonium citrate.	1 per cent citric acid.	N/200 HCl.	Taken off by crop.	N/5 HCl.	Ammonium citrate.	1 per cent citric acid.	NH <sub>4</sub> Cl.	N/5 CaCl <sub>2</sub> .	N/200 HCl.	Taken off by crop.
27	330	110	290	18	21	160	100	70	160	230	60	77
10	90	150	110	..	15	200	190	120	220	110	..	51
7	80	80	60	7	8	470	600	270	500	390	144	98
65	20	230	200	2	.5	170	190	90	210	220	50	66
80	90	150	70	5	6	220	260	170	230	340	170	41
63	200	60	320	25	14	430	420	270	430	260	84	62
93	160	300	350	25	6	330	850	120	390	150	46	37
121	130	230	340	7	13	160	180	70	160	120	35	34
98	350	100	270	..	2	190	190	50	160	90	..	10
44	160	50	70	..	2	70	90	20	50	70	..	4

In the soil most deficient in phosphorus pentoxide, the lowest result obtained is 50 parts per 1,000,000, being double that obtained by the best crop grown in 175 beds, while the result in the highest soil is sixteen times greater than what it actually was in the pot. Pots 63 and 93 are highest in available phosphate, but it does not appear high in the crop, owing to the deficiency of potash in these soils. The N/5 hydrochloric acid method grades pot 98 as first, while it is actually last. It grades pot 93 about half that of the lowest, while it is the highest. The ammonium chloride method grades the highest pot, 93, first, but

it grades one of the lowest pots, 65, second. The 1 per cent. citric acid correctly grades the highest pots, but grades the lowest as second. In the potash determinations, attention is called to the close agreement of the columns headed N/5 hydrochloric acid, and ammonium chloride. With the exception of those under the heading N/200 hydrochloric acid, the results in this table run from 10 to 200 times what it actually obtained in the crop, and in no definite direction.

Table E is incomplete owing to the lack of sufficient quantity of sample. In this table, in comparing pots 1 and 86, the phosphorus pentoxide is seen to be 105 against 74 in the N/25 acid. In the next weaker strength acid, the comparison is 63 to 40, then 35 to 26, then the figures reverse in N/200 and become 16 to 25. This last is just the result obtained by the crop. By a study of this table a number of such illustrations can be seen, which go to demonstrate that the fertility of a soil depends upon the quantity of phosphate contained in it, but upon the peculiar condition in which some part of that mineral exists.

By a comparison of Tables E and D, it was endeavored to obtain some foresight as to the successive crops. In cases where the soil is normally balanced in phosphate and potash, it will be seen that the phosphate represented as soluble in N/25 acid, very closely corresponds to that taken out by the three successive crops.

TABLE K.

Pot.	P <sub>2</sub> O <sub>5</sub> N/25 HCl.	Yield of three crops.
7	20	18
14	24	21
19	48	49
22	50	12
25	16	11
27	60	57
29	13	14
76	57	60
85	44	28
86	74	68

In pot 7, three crops have taken out 18 parts of phosphorus pentoxide, and the result for N/25 acid is 20. In pot 14 three crops take out 21 parts, and the N/25 acid shows 24. In pot 19 the three crops take out 49 against the result 48 as shown, and so on through the others. Pots 1, 18 and 63 show abnormally

high results in the N/25 acid, indicating an overbalance of phosphate.

While these results are not to be considered conclusive, yet, in the ten instances cited, the phosphate in all cases will be included within the phosphate soluble in N/25 acid, and in seven of these cases the results obtained by the three crops are practically identical with those obtained by the N/25 acid.

Special notice is directed to the fact that the proposed method as illustrated in Tables E and F, is intended as an interpretation of the yield of a crop, only in so far as the potash and phosphate are concerned. Two crops may make the same total yield of grain and straw, and still be very different in the amount of phosphate or potash that was taken from the soil. To illustrate, pot 162 in 1897 produced a crop analyzing 6.30 per cent. potash. Pot 164 in 1899 produced a total crop of the same weight as that in 162, analyzing only 1.35 per cent. potash. While pot 160 in 1899 produced a crop analyzing 0.31 per cent. phosphorus pentoxide, pot 164 in 1897 produced a crop analyzing 1.44 phosphorus pentoxide, the total crop weights being about the same. These pots are cited because they are the same original soil, the plots running high being fertilized. Here are crops the same in total yield, but one containing five times the plant food found in the other. We might refer to one crop as being diluted until it equals the other in weight. The question that presents itself is, Will a food so diluted be as valuable as an undiluted one, especially if the mineral matter is the desired constituent? If an animal is fed a ration of oats for the development of bone, on such a feed as that above referred to, it must eat five times as much, should it be fed on the poorer quality.

A crop deficient in the plant food desired, is a poor crop, even though large in bulk. While there are no instances recorded of where the price of oats was determined by its composition, rather than its bulk, still it is reasonable to infer that the one is more desirable than the other. If the soil is deficient in such a plant food, the deficiency should be supplied without regard to the effect upon the total yield. It is from this standpoint that the value of such a method may be viewed.

In order to obtain the efficiency of a soil in the matter of plant food supplied, the crop must not be looked upon as yielding so much grain, but the composition of the grain and straw must be

taken together. The formation of grain is dependent upon the season. The soil may have supplied the needed plant food, and it may have been taken up by the plant, but the transmigration of that food throughout the plant, is a process confined to the functions of the plant, which is to a large extent determined by the season. A good season may be represented as where the greater portion of the plant food has moved into the grain, while in a poor season, just as much plant food may have been taken from the soil, but remained, disseminated throughout the plant.

In pot 65 in 1895, the total crop ratio is 278, with phosphorus pentoxide expressed by a ratio of 5, while in pot 63 in 1897, the total crop ratio is 71, with phosphorus pentoxide equivalent to 15. The latter pot supplies a ratio of phosphate ten times that of the former.

It is evident that an overstimulated plant is quite different from the plant in its normal growth. The soil in pot 65, if not artificially, was naturally a very rich soil in nitrogen. The crop analysis shows 53 parts of nitrogen taken up, or nearly 20 per cent. more than the crop second highest in nitrogen of all the experiments that have been made in this work. Pot 63 in 1897 supplies three times as much phosphate, although it makes a total crop of but one-fourth that of pot 65. It would be expected that the crop in 65 was one in which the plant was enlarged with nitrogen-feeding, only that the ash is very high, showing that while potash and phosphorus pentoxide were taken in but very limited quantities, still some other mineral must have been substituted. However, these are "crude ash," and are very high in carbon, and not much can be learned from this.

In the Rothamsted soils the effect of fertilizer stimulant is apparent, even though none has been applied since received by the department. All except pot 170 had received nitrogen, pots 156 and 160 receiving nitrogen only. Pot 170, which had no fertilizer, shows a higher crop than 156 and 160. From a study of these soils it will be seen that the use of nitrogen increased the potash and phosphate but a trifle, while the addition of phosphate decidedly increased the phosphate taken up with no effect upon the potash. The addition of potash and phosphate shows a very large increase in both.

As before stated, the Rothamsted soils are so artificial that little reliance can be placed on them. These, with the previous

indications, point to stimulated growth as being more probably a dilution of the plant in its other constituents as compared with the constituents in the applied stimulant, rather than being an increase of the normal composition.

If the available plant food can be looked upon from the position in which it is attempted to illustrate in this paper, there are many suggestions presented. In Table F, pot 1 shows 16 parts of phosphorus pentoxide available, and 16 parts taken up by the crop, while for the next crop, 8 parts were available and taken up, to say nothing of that taken out by the intervening buckwheat crop. In pot 7, 7 parts were available and taken up the first year, while the second year showed the same condition. In pot 19, 18 parts were available and taken up, though the next year showed 12 parts available and utilized. In pot 27, 18 parts were available and consumed; the second year showed 16 parts still available. In pot 31 the 16 available parts were taken up the first year, and 18 found for the next year. So with pot 63. While pot 76 shows 31 parts available with 29 taken up by its crop, still the following year 13 parts are found again available, and the same with other cases will be noticed. It is seen that there is a decided resemblance between the phosphate present for a first crop, and that for the succeeding one, and not the reverse condition; that is, if a small quantity is taken up by one crop it will be increased in the second crop, owing to an accumulation, and if a large quantity is taken up by a crop, the next crop will be deficient, owing to a preceding exhaustion.

From the very marked illustrations, it is easy to believe, first, that the mineral food which a plant does take up is that which existed in the soil in an assimilable form at the time of planting, and second, that in the course of the plant's growth, a fresh supply of food will be rendered assimilable for the use of a succeeding plant, and that large crops will provide large amounts of plant food for a future crop, and small crops can only provide small quantities for future use. Hence, small crops induce small crops, and large crops induce large crops to follow up to the point of exhaustion.

It will be noticed that but little emphasis has been placed upon the total crop, and that it is the absolute amount of potash and phosphate removed which is considered. The writer has not been able to establish any relation between a crop and its com-



position, the ratios of phosphorus pentoxide to its respective crop varying as from  $\frac{1}{1000}$  to  $\frac{1}{100}$ .

Crops may be likened to poor and fat animals, the former having just as much mineral matter as the latter, while the total weights vary greatly. It is suggested that a crop obtains that quantity of mineral matter which is available, irrespective of an abundance or deficiency of nitrogen, the nitrogen increasing the weight through the additional formation of starch and such substances, and that the additional weight due to such carbohydrates, is much more subject to climatic influences than is that of the mineral constituents.

An effort was made to get some definite insight as to the changes which a soil must undergo, when subjected to the action of plant roots, and, if possible, to locate the changes at regular intervals. Such a condition is more easily seen when a minimum amount of soil is acted upon by a maximum amount of roots, and where the growth is forced, as in greenhouse culture. Accordingly, 40 pots, holding about 1 pint each, were filled with the same soil, and in each pot, 18 grains of corn were planted. At the end of two weeks, 6 pots were emptied, the corn plants and their roots freed of soil, all the soil put together as one sample, and all the plants and roots made into one sample. The roots were separated very easily, washed in a minimum quantity of water, the washings concentrated and mixed through the soil, which was then allowed to assume an air-dried condition before its moisture-free weight was obtained. The corn plants with their roots were then ashed and analyzed. The period at the end of the first two weeks will be known as B. After B, the periods were made weekly, the same operation of separation being repeated, until periods C, D, and E, had been reached. Here the plants had become pot-bound, and ceased to advance.

The original soil is designated as A. A sample of the corn seed used was analyzed in order to make the correction for the plant food added through this source. The plants and roots analyzed practically the same percentage of phosphate for each period. In no instance was all the phosphate recovered that had been added in the form of seed, about  $\frac{1}{10}$  of it being left. In potash, however, there was an increase as 2, 4, 6, 6, until about

four times as much had been taken from the soil as had been added in the seed.

In the soil analysis, the conditions of digestion were those as previously described, with the strength of acid ranging from N/200 to 2N. The results are tabulated in Table L.

A is the original soil, B the condition after a two weeks' growth, C a week later than B, D a week later than C, and E a week later than D. At B, there had been an addition of 23 parts of phosphorus pentoxide per 1,000,000 to the soil, as shown by the analysis of the plants and roots, while 60 parts of potash had been taken from the soil. At C, D, and E, the condition of the phosphate remained unchanged, while the potash increased to 130, then 225, after which the growth of the plants ceased, as shown by the potash remaining constant also the next period.

Period D will then be corrected for phosphorus pentoxide by subtracting the 20 parts which had been left from the seed, while the potash will be corrected by the addition of 225 parts, this much being taken up in excess of that which was added in the seed. Now if the original condition as shown in A be subtracted from the condition as shown in corrected D, it will leave a gain at the D period, which represents the transition of plant food into a more soluble state, in the course of four weeks under these most extreme conditions. After D, the plant's vitality was exhausted, and there is shown a shifting of the plant food in the reverse direction. There is evidence of a reverting, or fixation. At period E, there was no advancement over D, as shown by the phosphate and potash which was taken up. E is corrected, as was D, when there is found to be a loss over the original condition A, in phosphate, and a gain in potash. However, the potash gain has descended since the D period, so the difference in the conditions of potash at the periods D and E, represents a loss, while in phosphate, the gain at D, plus the loss at E, represents the transition of phosphate in a reverse direction. Still there is a total gain over all, represented by the transition of 22 parts of phosphorus pentoxide and 182 parts of potash into the range of solubility of 2N acid.

This points to a condition as existing in a great state of instability, though with a definite trend. It is a condition wherein the mineral compounds are constantly undergoing a change into



more soluble compounds, and with a tendency to revert before the compounds reach the point where they would leach out in drainage water.

It is not seen how so great a change in the solubility of minerals can be brought about through so weak an acid as is contained in the sap of plants. In this case, a five weeks' growth so affected the more insoluble minerals as to bring 182 parts per 1,000,000 of the potash compounds into the range of solubility of 2N acid. As a mere question of solution, the weak acid of the sap could not possibly exert so strong a solvent effect as that shown. It is easier to believe that the changes in the mineral compounds of the soil are due to the action of bacteria, which are stimulated by the excretions from the roots. On such a basis it would be easier to account for the benefit obtained, by the rotation of crops, and conclude that a good season meant nothing more than a sufficiency of moisture and warmth, in which such bacteria flourish.

The complete chemical and mechanical analyses, as illustrated in Tables B and C, have no bearing on the immediately available plant food, in so far as the writer is able to interpret. They have been studied from almost every conceivable point, and for every definite conclusion drawn, an equally indefinite one may be found under similar conditions. The analyses are presented in order that the work may be as complete as possible, and perhaps aid another who may care to study the data here presented.

In Table M, the order of descending magnitude, according to crop production, is continued.

In column *a*, the comparative producing ability is ascertained, according to the potash, lime, phosphorus pentoxide and nitrogen, being arranged in serial order up to 34. This order is obtained by taking the average grade of each soil in the four named determinations; that is, the soil in pot 1 stands first in potash, tenth in lime, eleventh in phosphorus pentoxide, and sixth in nitrogen, or an average of seventh, which, compared with the remaining soils, makes it rank fifth in serial order. In the same manner are the rest of the figures representing the serial order obtained.

In column *b*, a similar order is obtained, based on the standing in potash, phosphorus pentoxide and nitrogen.

In column *c*, potash and phosphorus pentoxide.

In column *d*, potash and nitrogen.

In column *e*, phosphorus pentoxide and nitrogen.

In column *f*, potash only.

In column *g*, phosphorus pentoxide only.

In column *h*, nitrogen only.

TABLE M.

Pot.	Serial order based on the comparative value of								Complete analysis.	Crop.
	K <sub>2</sub> O. CaO. P <sub>2</sub> O <sub>5</sub> . N.	K <sub>2</sub> O. P <sub>2</sub> O <sub>5</sub> . N.	K <sub>2</sub> O. P <sub>2</sub> O <sub>5</sub> . N.	K <sub>2</sub> O. N.	P <sub>2</sub> O <sub>5</sub> . N.	K <sub>2</sub> O. P <sub>2</sub> O <sub>5</sub> . N.	P <sub>2</sub> O <sub>5</sub> . N.	N.		
	<i>a</i>	<i>b</i>	<i>c</i>	<i>d</i>	<i>e</i>	<i>f</i>	<i>g</i>	<i>h</i>	<i>i</i>	
76	5	2	6	1	8	1	18	7	13	1
27	25	27	25	26	23	25	19	26	26	2
7	11	8	15	3	16	5	26	6	11	3
16	22	21	24	17	14	23	20	11	20	4
90	18	20	18	21	15	22	11	21	25	5
18	4	3	4	8	5	4	6	12	14	6
5	12	9	14	4	13	9	22	5	10	7
74	10	11	23	10	11	17	24	2	4	8
65	14	13	16	12	19	11	21	13	1	9
80	30	30	31	30	30	31	30	24	29	10
14	28	28	32	24	29	32	31	15	30	11
22	8	7	12	9	4	15	13	4	19	12
9	7	6	7	6	3	12	9	3	15	13
70	2	5	5	5	1	14	5	1	3	14
3	31	31	30	31	31	28	29	29	27	15
25	32	33	33	33	32	33	33	28	33	16
19	21	16	8	19	7	21	4	16	22	17
12	20	25	26	23	18	30	16	17	18	18
51	26	26	13	29	24	19	12	34	28	19
87	24	23	17	25	23	18	15	30	23	20
39	15	14	21	14	10	20	17	9	16	21
63	9	15	4	20	22	6	10	33	2	22
69	29	29	28	27	28	29	28	23	31	23
73	17	18	22	13	17	16	23	10	17	24
84	3	4	1	7	6	2	7	14	12	25
29	27	25	20	28	21	26	8	27	21	26
31	13	17	10	18	20	13	14	22	6	27
89	34	34	34	34	34	34	34	31	34	28
1	1	1	2	2	2	8	2	8	5	29
85	23	19	9	22	12	24	3	20	24	30
104	16	12	11	11	24	3	25	18	9	31
93	6	10	3	13	9	10	1	19	7	32
101	33	32	29	32	33	27	32	32	32	33
35	19	22	19	16	27	7	27	5	8	34
First half	9	9	9	9	11	8	5	12	8	
First third	4	5	2	5	3	5	2	5	4	
First fourth	2	3	2	4	2	4	1	4	2	

In column *i*, the serial order is based upon the complete mineral analysis.

When every mineral is taken into consideration, it is very evident that the soil ranking first in serial order will be the one with the largest amount of mineral matter dissolved, which is to say, that the soil lowest in insoluble residue will rank first in serial order. Accordingly column *i* is obtained direct from the column headed "Insoluble Residue," in Table B.

If these averages are arranged in two divisions, the serial order up to 17 should be found in the first division, in order that they may agree with the actual productive capacity, whereas, upon inspection, it is found that in every instance but half as many are found in the first division as should be there theoretically. If arranged in three divisions, the first division should contain eleven, ranging from eleven down. However, those found in the first division that come within this range, vary from one-fifth to less than one-half of the theoretical number. Again, if arranged in four divisions, in the first should be found eight, ranging from that figure downward, whereas, there is found but from one-fourth to one-half of the theoretical number.

At the bottom of the table are found the number that are found in each column in the first half, first third, and first fourth respectively.

The only deduction that can be obtained from this, is that the figures are remarkably adverse to the conclusion desired, as is well illustrated in pot 1 (which will undoubtedly rank first), according to all of the standards suggested in this table, while it grades but one-third of the maximum crop. The pot ranking lowest, will be unquestionably pot 89, when it is seen that the lowest and highest are consecutive, the lowest preceding.

It is believed that no such collection of complete analyses, on such a variety of soils whose agricultural value has actually been determined, has previously been presented, and that it would be difficult for them to be shown in a more unfavorable light. However, many such analyses are made, and in some cases even the mineral matter insoluble in acid is determined by means of fusion.

Such analyses might be of value in determining the geological origin, but this could be better done by an examination of the

rock, in the case of sedentary soils, whereas in the case of transported soils it could not be done in either case.

If it is expected that the digestion in strong acid will reveal what is to be the future state of fertility, it is suggested that the effect of weathering, upon this insoluble mineral matter, is so infinitesimal that it would be out of consideration in so far as agricultural purposes are concerned.

It will not be overlooked that the discussion throughout this paper, pertains to the oat plant only. As to whether the oat plant's habits and requirements of the oats are comparable with those of another plant, or whether the conditions of every plant must be established independently, is not within the scope of this paper. On lines similar to those followed in this paper, it would be possible to establish solvent conditions as representing the feeding ability of any plant, whereupon the desired crop would be specified when the soil sample is forwarded for analysis. If a diagnosis of a soil is made, it must be with reference to a specified plant, as plants vary so in the nature of their feed, and their ability to obtain it.

If plant food can be identified by a laboratory method, there is no doubt as to a method of procedure in the taking of soil samples from the field. A succession of similar depths should be taken in order to ascertain how deep the available food existed, and with this, compare the depth to which the feeding roots of the intended crop are known to penetrate. For actual practice, the writer has constructed a very simple form of sampling cylinder, made out of 7-inch wrought-iron pipe. The pipe is cut 6 inches in length, and turned down to a thickness of  $\frac{1}{16}$  inch, leaving a collar on one end, to strengthen and drive upon, while a cutting edge is turned at the other end. This makes a strong cylinder weighing about 4 pounds. The cylinder is driven down to the top, and the enclosed soil taken out. The soil is dug from around the sides of the cylinder as it is driven down for the second 6 inches, and so for a third 6 inches. The separate portions are weighed and subsampled for analysis, and from such data the pounds per acre of plant food to definite depths are obtained.

It is clearly obvious that the depth to which the plant food is supplied to the plant, is of great importance. To fix a definite depth at which a soil should be sampled, is about the same as at-

tempting to fix a definite depth at which a plant shall feed. If the first 6 inches of one soil should contain, say 20 parts per 1,000,000 of available phosphorus pentoxide, and the second 6 inches should contain none, and in a second soil the first 6 inches should contain 10 parts, and the second 6 inches also 10 parts, it is reasonable to suppose that in the growth of plants, which will feed to a depth of 12 inches or more, two such soils will be equally fertile.

The more divisions into which a soil sample can be divided, the more data there will be for study. If the successive depths could be reduced to 3 or 4 inches (it being understood that definite areas are taken), and a series of samples taken until the vanishing point of the available food is reached, from such data a curve could be drawn which, if compared with the root system of a plant, would illustrate the amount of available food which could be assumed as being present.

However, if it is limited to two, or even one sample, let the total depth be that to which the intended crop is known to feed. If it is intended to estimate the amount of plant food which is in an acre to the depth of a feeding crop, say 12 inches, and all of the available food chances to be in the first 4 inches, it is immaterial as to whether the soil be sampled to a depth of 4, 6, 8, 10, or 12 inches, as the final calculation will be the same in each case. Consequently, if it is not known to what depth the available food exists, if a single sample to the depth of 12 inches be taken, it covers all doubt, and with no disadvantage in case the available food does not extend so far.

For an illustration, Table N is an arrangement of the first and second 6 inches of the same soil, with the phosphorus pentoxide and the potash of the upper and lower samples arranged accordingly.

In soil *a* the first 6 inches were in pot 1, with the second 6 inches in pot 31, the others being similarly arranged. The phosphorus pentoxide in soils *a* and *d* is seen to be equally distributed to at least a depth of 12 inches, while in soils *c* and *f*, practically all of the phosphorus pentoxide is found in the first 6 inches. In soils *b* and *e*, there is practically none in the first 6 inches, and, as would be expected, none in the second 6 inches.

If it is undertaken to place a comparative value on these soils with respect to the phosphorus pentoxide, let it first be assumed



TABLE N.

Surface soils and their respective subsoils compared.

[Parts per million.]

Soils.	Pot.	P <sub>2</sub> O <sub>5</sub> .	K <sub>2</sub> O.
<i>a</i>	{ 1 31	16 16	65 20
<i>b</i>	{ 3 35	2 1	102 1
<i>c</i>	{ 19 51	18 3	235 76
<i>d</i>	{ 63 93	25 25	84 6
<i>e</i>	{ 69 101	1 1	47 31
<i>f</i>	{ 86 115	25 1	116 16

that the intended crop can not feed to a greater depth than 6 inches. Then soils *a* and *c* are equally fertile, as will be also *d* and *f*. If it is assumed that the intended crop will feed to at least a depth of 12 inches, the soil *a* will be one-half more fertile than *c*, while *d* will be two times as fertile as *f*, soils *b* and *e* being deficient in both cases.

Similar comparisons may be made with the potash.

In the continuation of soil study, assume that the available plant food rarely extends to a depth of more than 12 inches, and that plants penetrating below that depth, do so for the purpose of obtaining moisture. If such assumptions should become facts, it would be a simple matter to obtain an accurate sample by sampling through a definite area to a depth of about 12 inches, weighing the total sample, mixing and taking a definite portion as a subsample for analysis. In such a case, the exact depth to which a sample is taken would be of small importance. It might range from 10 inches to 10 feet without variation in the result, provided the area over which the sample is taken, is accurately defined, and a definite portion of the thoroughly mixed total sample taken.

TABLE O.  
Index of samples studied.

Pot.	State.	Type.	Strength sol. for N/10 filtrate.	Pot.	State.	Type.	Strength sol. for N/10 filtrate.
1	California	vir. sur.	N/8.5	73	Indiana	cul. sur.	N/7.4
3	Illinois	"	N/9	74	Iowa	"	N 6
5	"	"	N/7	76	Kansas	"	N 8.4
7	Kansas	"	N/8.3	80	Michigan	"	N/9
9	Indiana	"	N/7.2	84	Montana	"	N 6.1
12	Massachusetts	"	N/8.7	85	New York	"	N/9.6
14	Michigan	"	N/9	86	Oregon	"	N/8.5
16	Missouri	"	N/8.5	87	S. Dakota	"	N/6.6
18	Montana	"	N/8	89	Texas	"	N/9.4
19	New York	"	N/9.1	90	Wisconsin	"	N/8.8
20	Oregon	"	N/8.4	93	California	cul. sub.	N/6.6
22	S. Dakota	"	N/8.4	101	Illinois	"	N/9.1
25	Texas	"	N/9	104	Kansas	"	N/9.2
27	Wisconsin	"	N/8.2	115	Oregon	"	N/6.5
29	Maryland	"	N/9.5	117	"	"	N/6.1
31	California	vir. sub.	N/6.3	156	Rothamsted	W10a	N/6.2
35	Illinois	"	N/8	158	"	W11	N/6
39	Iowa	"	N/6.3	160	"	B1a	N/6.7
51	New York	"	N/9.3	162	"	W13	N/6
63	California	cul. sur.	N/6	164	"	B2a	N/6.7
65	"	"	N/9.5	166	"	B3a	N/6.7
69	Illinois	"	N/8.5	168	"	B4a	N/6.7
70	"	"	N/5.5	170	"	W3	N/5.4

### NEW BOOKS.

METHODS OF CHEMICAL ANALYSIS AND FOUNDRY CHEMISTRY. BY FRANK L. CROBAUGH, M.S., Cleveland, O. Published by the author.

The analyst, or any person who intends to become an expert analyst, needs to have his methods at hand concisely stated, with all details verified by himself or by an author who has tested the methods thoroughly. In a work recently published by Mr. Frank L. Crobaugh, of Cleveland, Ohio, may be found a collection of selected methods especially in use in analysis of iron and steel, which have been thoroughly tested by the expert hand of the author. On account of the varied experience of Mr. Crobaugh in iron laboratories, in iron and steel plants and in his own business, his compilation of these methods will be of great service to any chemist engaged in similar work.

In Part II of this work will be found a more complete statement of the principles and methods of foundry chemistry, than can be found elsewhere. Foundrymen are beginning to appreciate the importance of a more thorough knowledge of the chemical composition of pigs and castings, and of the chemical changes involved in foundry practice. They will find this book very useful in their daily work.

C. F. MABERY.





*J. W. Clarke*

# THE JOURNAL

OF THE

# AMERICAN CHEMICAL SOCIETY.

---

## THE DEVELOPMENT OF CHEMISTRY.<sup>1</sup>

By F. W. CLARKE.

Received January 6, 1902.

THE American Chemical Society exists for the advancement of chemical science, and the betterment of the chemical profession. Every member of it is supposed to contribute his share of thought and energy to the accomplishment of these ends; and so its work is prosecuted along many lines of activity. During the past ten years the growth of the Society has been most remarkable, and the diversity of its interests is well shown in the pages of its journal. The once doubtful experiment of organization has justified itself by success, and there are no longer any apprehensions as to the future. The Society now stands before the world well established, well recognized, active, and vigorous; its days of weakness and danger are over; we can look forward with confidence to greater prosperity, to larger growth, to steadily increasing usefulness. All chemistry is our province, whether it be organic, inorganic, theoretical, physical, or applied; and the narrowness of specialism finds its best antidote in the varied interests of our meetings. To promote science and to uphold the dignity of our common profession are the objects which bind us together.

Optimism is a good thing, but it needs to be tempered by rea-

<sup>1</sup> Presidential address delivered at the Philadelphia meeting of the American Chemical Society, December 30, 1901.

son. Hopefulness and enthusiasm are fine qualities, but the restraint of common sense should keep them within bounds. Too much complacency is dangerous, and on occasions like this we may well pause in our gratulations over past achievements, to ask ourselves whither we are tending. As chemists, we owe something to the science which we represent, and the debt is one which can never be discharged absolutely. That we have done much is evidence that we can and should do more ; as a society and as individuals we may well look about us and strive to see which way the path of duty lies. We cannot appraise the future, but we must help to make it. Only by acting with intelligent forethought can we hope to advance creditably.

Retrospection is the one safe basis for prophecy. The history of science is full of suggestions for the days to come, and even if we do no more than avoid the repetition of mistakes, we shall gain much from the study. Great as the past has been, we can make sure of something better still, looking confidently forward to more perfect knowledge, to larger opportunities for research, and to wider recognition in the republic of learning. Let us see how chemistry has developed hitherto, and how we can improve her present condition.

A little over a century ago chemistry was hardly more than an empirical art,—a minor department in the broad field of natural philosophy. There were no chemists in the professional sense of the term; and no laboratories worthy of the name ; that is, no buildings were planned and erected for chemical purposes alone ; but chemical investigations were conducted in any room which happened to be available, with a disregard for convenience which would be intolerable to-day. Even at a later period the marvelous researches of Berzelius were performed in a laboratory which was essentially a kitchen. If we use the word in its true sense, the earlier chemists were amateurs ; that is to say, men who labored for the love of truth and without ulterior professional motives. Priestley was a clergyman, who regarded his voluminous theological writings as more important than his contributions to science. Scheele was an apothecary ; Lavoisier was a public official with multifarious duties ; Dalton was a schoolmaster and arithmetician. Before these men and their contemporaries, a vast unexplored territory was outspread, and no one could suspect what hidden riches might lie beneath its surface. Lavoisier, with

his emphasis upon quantitative methods; Dalton, with his atomic theory; Davy, the discoverer and definer of elements; and Berzelius, with his genius for system and his untiring industry in the accumulation of details, opened the main roads into the new empire. Specialism in chemistry was practically unknown; all portions of its domain seemed to be equally inviting; but inorganic problems were perhaps the most obvious, and, being easiest to grasp, received the greater share of attention.

There were, from the beginning, two great stimuli to chemical research: the intellectual interest of the problems to be solved, and the practical utility of many discoveries. Both forces were essential to the rapid development of our science; neither one alone would have been adequately effective. Economic considerations, taken by themselves, help but little towards the symmetrical organization of scientific knowledge, for the practical man has usually a limited, although very direct purpose in view, and may not wander far from his main issue. On the other hand, the purely scientific investigator can rarely exercise his full powers without a certain measure of popular support and encouragement, to which the expectation of usefulness contributes. That discovery must precede application is obvious; that systematic knowledge outranks empiricism is also clearly true; but theory and practice react upon each other, and it is only when they work harmoniously side by side that the best results are attainable. The purist in science too often overlooks this fact, and fails to recognize his enormous debt to industry. The commercial demand for chemical data was an important factor in the establishment of our profession, and from it we derive a large part of our resources. At bottom, however, the demand is essentially selfish; and the manufacturer who seeks chemical aid, nay, even the technical chemist himself, is not uncommonly forgetful of his obligations to pure research. Every chemical occupation is based upon discoveries which were made without thought of material profit, and which sprang from investigations undertaken in the interests of truth alone. Even theory, which the ignorant worker affects to despise, has its place in the economic world, and the indebtedness of the coal-tar industry to Kekulé can hardly be overestimated. Without theory science is impossible; we should have, instead, only a chaotic anarchy of disconnected facts, a body without a soul. Theory is to science what discipline is to an

army ; it implies system, method, and the intelligent direction of affairs ; it is the coordination of knowledge, through which the experience of others becomes best available to us. The victories of research are rarely accidental ; if they were, then the untrained tyro would have an equal chance of success with the greatest masters. Among ourselves, these considerations may be commonplace, but they are opposed by certain popular misconceptions which hinder our advancement and work mischief to our cause. *Cui bono* is the one question which science cannot ask.

Four agencies have been chiefly instrumental in building up the chemical structure of to-day ; namely, private enterprise, the commercial demand, governmental requirements, and the extension of scientific teaching in the universities. Under the first of these headings the foundations of chemistry were laid, and the researches of Cavendish upon the composition of the atmosphere, may be taken as types of the class. Unfortunately, however, the men who combine the requisites of wealth, leisure, the inclination and the ability for scientific investigation are few in number, and the output of their labors is relatively small. Still, we must admit that the work so accomplished is often far above the average in quality, and that if it were to cease, our science would be much the poorer. Its motive is always high, and unaffected by any annoying pressure from necessity ; its objects are purely scientific.

Seen from the commercial side, chemistry presents quite another aspect. Questions of utility are now paramount, and the advancement of science as such has become a secondary affair. The manufacturer seeks to improve his products, or to cheapen his processes, and calls for information which shall enable him to do so ; specific industrial problems require immediate attention, and each one is taken by itself, regardless of its broader philosophical bearings. From these conditions a certain narrowness must follow ; no time can be wasted over considerations not directly related to the matters in hand, for the success or failure of a great enterprise may depend upon the quickness with which the obviously essential work is done. As against this urgency of demand, no just criticism can be offered ; we may only ask that it shall be reasonable, and that science shall be treated less as a servant, and more as a faithful ally. The commercial chemist owes something to his profession, as well as to his employer ; and his industrial



duties ought not to be incompatible with his responsibilities as a scientific man. The education of the manufacturer is one of the functions which he has to perform, and it is one which is not always easy of accomplishment. Two points of view have to be reconciled : self-interest is on the one side, the benefit of science on the other.

Several difficulties beset the pathway of applied science, and interfere with the work of its practitioners. The limitations of the field have already been suggested, but a more serious obstacle to progress is found in the secretiveness of the employer. The industrial chemist cannot publish his researches, or at best can publish little ; he therefore fails to receive before the world the credit which is his due, and science as a whole is the loser. A secret process, an unpublished investigation, adds nothing to the sum of human knowledge, and it represents a policy which is both short-sighted and unwise. It often covers ground which has been well covered before, and in that case it stands for misdirected effort, for wasted energy. I have seen, under the seal of confidence, a "secret process" which had been in print for twenty years ; its too practical inventor, ignorant of the literature of his subject, had worked out his methods independently ; had he consulted others he might have saved both expense and time. On still broader grounds I believe we may claim that the publicity of science is more economical than the current exclusiveness. Where several competing establishments produce the same class of goods, each one tries to hide its workings from the others. Each, therefore, gains only that new knowledge which it can develop by itself, whereas with greater wisdom it might profit by the experience of all. Secrets will leak out, in spite of precautions ; a full interchange of thought merely anticipates the danger, and at last the manufacturer may find that instead of suffering loss, he has really received much for little. Possibly the combination of industries under the so-called "trusts" may act favorably upon scientific research, for when rivalry ceases, the incentive to secrecy disappears also.

If we study the reaction between science and industry at all closely, I think we shall find that an economic revolution of remarkable importance is well under way. Like all the greater social movements, it is going on quietly, without noise or bluster, but it is nevertheless far-reaching in its effects. Manufacturing,

once a matter of empirical judgment and individual skill, is more and more becoming an aggregation of scientific processes, a system in which accurate quantitative methods are replacing the old rules of thumb. Exact weight and measure are taking the place of guesswork, and by their means waste is diminished and economy of production is insured. I can remember the day when few establishments in America gave regular employment to chemists; now laboratories are maintained in connection with nearly all productive enterprises, and the demand for scientific service, which was formerly sporadic, has become well-nigh universal. A railway system, making contracts for supplies, does so upon the basis of chemical reports; and the work is performed in its own offices by experts who are permanently retained. In the management of an iron furnace, ore, flux, fuel, and product are analyzed from day to day, by methods of amazing rapidity and considerable exactness. Fertilizers are sold upon chemical certificate after preparation under chemical rules; sugar is refined by chemical processes, and taxed according to chemical standards; medicine is enriched by new remedies of chemical origin; in short, our science touches every productive industry at many points, and aids in its transformation. Metallurgy is becoming more and more a chemical art; photography, a modern science, rests upon chemical foundations; with the aid of the electric furnace new chemical industries are springing into existence; and every one of these agencies reacts upon the chemist, by increasing the demand for his services and his wares. In Germany this development of applied science has gone the farthest; and in that country a single establishment may employ from fifty to more than a hundred chemists in its regular work. Some of these men are analysts merely, but others are engaged in systematic research, which has both science and industry in view. This appreciation of research as such is something to which few of our American manufacturers have attained; and it marks the highest step yet taken in the line of industrial progress. The modern era began when hand labor, which means individualism, gave way to machinery; but the machine is a symbol of organized intellectual power, and science is the bed-rock of its foundation. Chance and supposition are out of place in the industrial world of to-day.

Turning now to the governmental side of science, we find that the services of the chemist are everywhere in demand. Every

civilized government now maintains chemical laboratories, and for purposes of the most varied kind. The accuracy of the coinage is determined by the assayer ; supplies for public use are tested by analytical methods ; taxes are assessed in terms which need chemical interpretation ; the armor of the battleship and the explosive of the torpedo depend for their efficiency upon the skill with which our work is done. The sanitation of cities ; their water supply ; the disposal of sewage ; the effectiveness of anti-septics ; the quality of gas for lighting or of asphalt for paving ; the warfare against the adulteration of food ;—all of these questions are essentially chemical in character, and are, or should be, settled in the official laboratory. The aggregate of this work is something enormous ; and yet, like commercial chemistry, it has utility, not science, in view. Science may advance because of it, but that is not the main purpose ; the application of existing knowledge to public uses, and the creation of new knowledge are two distinct things. Here again chemistry is a servant, nothing more.

Throughout the scientific bureaus of the government this secondary character of chemistry appears. In the Geological Survey it is an aid to geology ; in the Department of Agriculture, agriculture is to be advanced ; in the medical service of the army or the navy, the interests of medicine come first. Chemistry for its own sake has as yet little or no governmental support ; astronomy is encouraged, geology receives assistance, the biological sciences are given opportunities for growth ; but our profession is merely utilized, without thought of its significance, its laborers being too often overworked and underpaid.

In an incidental way, however, the governmental laboratories accomplish something for pure science, albeit with little direct encouragement and in spite of difficulties. The official chemist, unlike his commercial brother, is not always crowded for time ; his work can be done in a somewhat more leisurely manner, for it is unaffected by any demand for immediate financial returns ; and so abstract researches, if they bear in any way upon the problems which are assigned him, are sometimes within his reach. Chemistry owes much to investigations of this class ; and the papers which issue from official laboratories are by no means to be despised. Good work is done, but there ought to be more of it ; research should become a recognized duty, rather than an

employment for spare time. It would be well if every government could be made to see that the use of science implies the encouragement of science, for then we might hope for the establishment of laboratories for purposes of investigation alone. To this proposition I shall recur later.

We now come to the fourth of the agencies by which chemistry has been developed, the educational, and this is the most important of all. Scientific research has become a definite function of the modern university, wherein the creation of knowledge is given equal rank with the distribution thereof. Education to-day differs from the education of former times, in that a lower place is given to mere authority ; it goes more to the foundation of things, and so secures a foothold from which it can build much higher. Research, both for its own sake and as an example to the student, is now expected of the teacher ; his pupils, coming face to face with the limitations of knowledge, are shown the problems which demand solution, and are taught something, by practice and by precept, of the manner in which they can be solved. The student learns that science is a living growth, and that every earnest, sincere, well-trained scholar can do something towards its development. If we examine the chemical journals of the nineteenth century, we shall find that by far the larger part of the discoveries therein recorded were made in the laboratories of universities or schools. Even in our own journal, with all of its contributions from technical and official sources, over sixty per cent. of the communications published are of this class. The significance of this fact, however, must not be overestimated ; we should remember the restrictions under which the technical chemist labors, whereas to the university professor publication is almost as the breath of life. His professional standing, his chances of promotion, are profoundly affected by the amount and character of the work which he puts forth ; silence, to him, means the possible reproach of inactivity ; he must publish or remain obscure. Furthermore, we must not forget that the teacher owes a debt to technology which can never be repaid. The commercial demand for applications of science has enlarged the field of education, by compelling the establishment of polytechnic schools. These institutions, all of them of recent date, give employment to thousands of instructors ; they supplement the universities, they multiply the facilities for scientific work,

and from them, too, there flows a steady stream of contributions to knowledge, to which the chemist is adding his full share.

Apart from the freedom to publish, the university teacher has one great advantage over the technical man. He is not confined to any limited field of operations, such as the chemistry of soap, of iron, or of coal-tar; the whole domain of the science lies open before him to explore where he will. The possible utility of the work need not occupy his mind; he can attack any problem he chooses, and from any point of view. And yet, with all incentives to breadth, his researches may still be tainted with narrowness, for the inevitable tendency to specialize puts its restrictions upon him. It is much easier to be a physical chemist, an organic chemist, an agricultural chemist, or an analyst, than it is to be a chemist; and chemists, in the larger sense, are few. It was Berzelius, I think, who said that he was the last man who could ever know all chemistry, and the saying was both wise and true. Sixty years ago our science could be mastered in its entirety by one industrious student; to-day it is so vast that subdivision is necessary. Still, special research is not incompatible with breadth of view; every chemist should understand the nature of the great central problems; he should stand high enough to overlook the field, no matter how small a corner of it he may prefer to cultivate personally. Broadness of mind does not imply a scattering of resources, a futile waste of opportunity; it means an intelligent appreciation of all good scientific work, whether it be within our own bailiwick or elsewhere. To exalt one specialty at the expense of others, to claim supremacy for our own small interests, indicates a self-conceit which is both mischievous and absurd.

With so many opportunities for research, and with numberless problems in sight, chemistry should have grown according to some law of symmetry, giving us to-day a well-balanced and harmonious whole. History, however, tells a different tale. The science has expanded enormously in some directions, and advanced slowly in others; a glaring disproportion is the result. For this condition of affairs there are two reasons: lack of coordinated labor and the influence of fashion; for there are fashions in thinking, just as there are in dress, and only the most original minds can escape from their domination. Theoretically, every investigator is free to follow his own bent; practically, his

course is shaped by a complexity of circumstances. The line of least resistance is the easiest line to take, and in science that is determined by temporary conditions. Certain researches have been fruitful; and so, like miners flocking to a new camp, we are tempted to enter the same field, rather than to play the pioneer elsewhere. The greatest prospect of immediate success is the power which attracts us. Through influences of this kind chemistry has developed unevenly, with one side overcultivated and another suffering from neglect.

To illustrate my meaning. I do not wish to underrate the importance of organic chemistry, nor to question, in the smallest degree, the value of its achievements. Its interest, its attractiveness, the beauty of its methods, its profound influence upon chemical theory are all admitted; and yet it has received, it seems to me, an undue share of attention. During fifty years a large majority of all chemical investigators devoted themselves to this one branch of chemistry, leaving only a few workers to occupy other fields. Organic chemistry was the fashion; in it reputations were easiest made; the great professional prizes, the best positions, went to its devotees.

Now, in spite of all that organic chemistry has accomplished, we may fairly admit that chemical research should have a broader scope. Carbon is but one element among many; and all must be considered before we can be sure that our interpretations of chemical phenomena are sound. Special cases are easily mistaken for general laws; and to such errors we become liable when we confine our studies within too narrow bounds. Fortunately for chemistry, a broadening process has begun; and the prospects for the future are most encouraging.

During the past ten or fifteen years two movements have gained headway in the chemical world. One is marked by the revival of interest in inorganic problems, the other by the development of physico-chemical research. To a certain extent the two have much in common; each one is aided, I might say fertilized, by conceptions borrowed from the organic field; both are already fruitful to a remarkable degree. Independent journals devoted entirely to inorganic or physical chemistry, have come into existence, and investigators of the highest rank fill them with contributions. It is not my purpose to discuss either movement in detail; I mention them as symptoms of a more liberal spirit in re-

search, as indicating the commencement of a new era. Physical chemistry in particular is becoming the center of interest; laboratories are built and equipped for its benefit alone; it bids fair to surpass even organic chemistry in its dominion over chemical thought. One danger, however, confronts it,—the danger of self-exaggeration, stimulated by overpopularity. Physical chemistry, to achieve the best results, has need of data drawn from other lines of chemical research; if they are neglected, it in turn will suffer. Even now too large a proportion of its votaries are working in one field; that is, on questions growing out of the current theory of solutions, and other subjects fail to receive the attention which they deserve. This state of affairs, this lack of proportion, is doubtless only temporary, for towards physical chemistry all chemical theories converge, and no phase of it, therefore, can long escape consideration. The very nature of physical chemistry implies a prohibition of narrowness; broad conceptions and deep insight are essential to its being.

When we consider the complex influences, the varied demands, through which chemistry has developed hitherto, we can only wonder at the outcome. Under the circumstances, a symmetrical growth was impossible; the marvel is that so much could have been accomplished. Out of unorganized, uncoordinated, individual efforts a true science has come into existence, equal in dignity to any other within the domain of learning. All science is defective, but in its very imperfections we find its greatest charm. Through them alone effort becomes possible; a wise discontent on our part is the first condition for progress. If all were known, research would come to an end; nothing could arouse our curiosity; the human mind would atrophy for want of exercise. The search for truth is better than the truth itself,—if I may be allowed thus to paraphrase the well-known words of Lessing. In what direction, then, shall we pursue our search, and with what promise for the future? What are the needs of chemistry?

Pardon me, now, if I apparently indulge in commonplace; if I cite some considerations of almost alphabetic simplicity. Fundamental principles lie so close to our eyes that they are easily overlooked; and from negligence of that kind, misdirected effort may follow. We must review our lessons sometimes in order to make sure of what we really know. In the first place it is well

to bear in mind that chemistry and physics are not sharply distinct ; that they are two parts of the same great body of truth ; and that neither can be studied to the best advantage without aid from the other. Both rest upon the same two basic doctrines, the conservation of energy and the persistence of matter, conceptions which supplement each other and which give our work its philosophical validity.

If we try to consider chemistry by itself, to conceive of it as an independent branch of learning, we shall find that it has but one fundamental problem, namely, the study of chemical reactions. From certain kinds of matter certain other kinds are produced ; and we merely investigate the laws which govern the transformations. If we prepare new compounds, we discover that such and such reactions are possible, and we describe their products. If we are interested in chemical equilibrium, we seek to determine the limits between which a given change can occur. Even our notions of chemical structure and atomic linking are but devices through which reactions and their products may be coordinated. In every case the reaction is the ultimate object of purely chemical research, and we try to ascertain its laws. Beyond this we enter the realm of physics ; we describe each kind of matter in thermal, optical, electrical, mechanical, and gravitational terms, and we discuss the phenomena of chemical change in similar phraseology.

Let us take, for example, any reaction whatever, and see what its *complete* investigation signifies. At once the problem will resolve itself into four parts, two statical and two dynamical, not one of which can logically be neglected. First, there are the substances which enter into the reaction ; secondly, the physical stimulus, thermal, electrical, or actinic, which starts the reaction ; thirdly, the phenomena which occur during the reaction ; and finally, the substances produced by the reaction. An initial state of equilibrium is disturbed by some application of energy ; transformations of energy take place, and in a final state of equilibrium the process comes to an end. Through a mixture of gases having certain physical properties we pass an electric spark ; they unite to form a liquid with different physical properties, the process being attended by a change of volume and great evolution of heat. The fact of union is chemical ; the other phenomena are physical ; and the two sets of considerations are so interlaced that we are



compelled to take them together. Intellectually we can discriminate between them, but the line of demarcation is essentially ideal. The chemical composition of matter cannot be studied apart from its physical relations, nor discussed without the aid of physical terminology.

It is easier to preach than to practice ; to say what should be done than to do it. Between the theoretical statement of a problem and the practical method by which it may be solved, there is a profound gulf, over which a direct passage is perhaps impossible. No reaction has yet been exhaustively studied on the lines which I have laid down, and possibly none ever will be, for the difficulties in the way of such a research are almost insuperable. Of all the snares which nature sets before our unwary feet, that of apparent simplicity is the most deceptive. Honest complexity, evident at sight, we may hope to overcome ; it is the unseen obstacle which baffles us. In the present instance a prime difficulty is the definition, the isolation of a reaction by itself, apart from other chemical changes. Nearly every reaction which we can observe is, in reality, a complex of several reactions,—a series of steps, some of which may easily escape our notice. We measure certain phenomena only to find at last that our result is an algebraic sum, and that we have more unknown quantities than equations. We cannot solve our problem until these factors have been recognized and separated.

To study individual reactions then, except for the determination of definite, special phases, is not the best mode of procedure; chemistry would advance but slowly were we restricted to such a method. In ordinary chemical research, in the work of the compound-maker for example, the initial and final stages of a series of reactions are investigated, and in that way valuable data are obtained. But the aim of science is not so much to amass facts, as to connect them by laws and principles ; and the more general the latter become, the greater is their intellectual value. We can not build, of course, until we have the materials, but between brick-making and architecture the difference is great indeed.

Leaving now the apparently simple, and turning to the visibly complex, let us see whether we cannot attack all reactions collectively, and in that way reach a more general statement of our real, experimental problems. All reactions display the same fundamental phenomena ; namely, changes of composition, changes of

properties, and transformations of energy ; if we can classify our data under these categories, we shall begin to see more clearly the road we are to follow.

Now, recurring for a moment to the analysis of a single reaction, we may consider its two statical terms, the nature of the substances with which we begin and end. In any particular instance these questions are special and limited ; but through them we discover facts which may be grouped with others of like kind. Presently we shall reach the discrimination between elements and compounds ; and sooner or later we shall find ourselves face to face with one of the ultimate problems of all science,—the nature of matter itself. In this problem all questions of chemical composition come to a focus ; it goes back of the reaction to the substances which react ; but it belongs equally to physics, and its essential details admit of description only in physical terms. Chemistry, however, is doing the most towards its solution, for it is through chemical researches that variations in the composition of matter are best explained. The indebtedness of chemistry to physics is thus fully repaid.

What is matter ? Is it continuous or discrete, atomic, or made up of vortex rings in the ether ? These questions admit of only partial answers, and doubtless their final solution is unattainable by man. They are, nevertheless, perfectly legitimate questions for science to ask ; and a tentative reply, of great practical value, is given by the atomic theory. Whether it be true or false, whether the chemical atoms are ultimate or divisible, this doctrine is the connecting thread upon which our profoundest generalizations are strung, and it is hard to see how we could do without it. Once a mere speculation of philosophy, Dalton gave it quantitative meaning ; and from his day to the present every great advance in chemical theory has found its clearest statement in atomic terms. Chemical equations and formulas ; the laws which correlate the density of a gas with its composition ; the law of Dulong and Petit ; our ideas of valency and molecular structure ; the periodic law ; and the relations of stereochemistry, are all connected by the atomic theory, whose retention in science is therefore fully justified. It may not be beyond criticism ; indeed, it should be criticized ; but it would be the utmost folly to abandon the theory before something better has been framed to take its place. Vague and unsatisfactory are the attempts which

have so far been made to supplant it. Physics, unaided by chemistry, may reach the conception of molecules; but the subdivision of the latter, the identification of their parts, is the function of the chemist alone.

If the nature of matter is the first element in the study of chemical reactions, the nature of chemical union is the second. If combination consists in a juxtaposition of atoms, what is the force which draws and holds them together? Whether we can answer this question or not, we may investigate the laws under which chemical action is operative, and so develop an important portion of physical chemistry. Problems of chemical equilibrium, of limiting conditions, of affinity and the speed of reactions, all come under this heading, and these are fit subjects for investigation in the laboratory. For instance, chemical action is impossible at very low temperatures, and at sufficiently high temperatures all compounds dissociate; each reaction, therefore, is confined to a certain part of the thermometric scale, which in many cases is measurable. In other words, chemical change is a function of temperature, no matter what additional factors its complete study may involve. It may also be effected through the agency of electrical or actinic impulses; and here again experimental research has a wide field. Were physical chemistry restricted, as it is not, to this class of investigations alone, it would still have abundant occupation. These illustrations are enough for my immediate purpose, but they could be multiplied indefinitely.

Directly growing out of these two fundamental questions, and partly identifiable with them, are two other problems of great generality and importance. First, what laws connect the properties of compounds with their composition? Secondly, what laws govern the transformations of energy during chemical change? Along each of these lines a large amount of work has been done, mostly empirical; and some regularities, some minor laws, are already recognized. Systematically, however, neither field is well known, and both offer rich prizes to the investigator. Great masses of more or less available data now exist; but rarely do we find any group adequately developed. The determination of constants, or the measurement of thermochemical relations, is tedious in the extreme; but a vast amount of such work needs to be done under some definite system or plan. At present we have a datum here and a datum there; some one in Germany

makes a few measurements, some one in France, in England, or in America makes a few more ; but seldom is there any attempt at cooperation, and the isolated facts do not always fit together. The thermochemical data are especially difficult to determine accurately, and still more difficult to discuss in such a way as to develop any clearly defined law. Indeed, thermochemistry, of late years, has fallen out of favor, for to many chemists, despite its promise, it seems to lead nowhere. But laws must exist under all these troubling questions, and we cannot despair of their discovery. We can accomplish little, however, unless we consider each of the four great fundamental problems with reference to the others, for they are separable only in theory. Scientific research is not linear, step following step in regular succession ; it is a network, rather, whose interlacing threads are woven into patterns of infinite variety. We trace individual fibers, we see, more or less clearly, a part of the design ; and this is the most that any one of us can ever hope to do.

Now, whether we regard the fundamental questions of chemistry as four in number, or condense them into two, we can use our classification as an aid to research. Success in the latter means a wise selection of problems, a choice which is conditioned by our strength and our resources ; but the first step is to understand the bearings of what we are trying to do. Whether our purposes are modest or ambitious, our work must have an influence upon that of others, and the broader the plan upon which it is conceived, the better the outcome will be. One bullet well aimed is worth more than a volley at random. One fact with a purpose outweighs a hundred scattering observations. We may well ask, therefore, what investigations are most needed by chemistry to-day ?

First, as to the nature of matter, with all that that question implies. Taking all kinds of matter into consideration, and starting with the established distinction between elements and compounds, it would seem to be obvious that work is most imperatively needed where our information is least complete. Some elements, some classes of compounds, have been much more exhaustively studied than others ; they, therefore, can best bear a temporary neglect, our attention, in the meanwhile, being concentrated elsewhere. I do not mean by this that any kind of research should cease, only that each department should assume

something like reasonable proportions. To organic chemistry, for example, we are indebted for many methods of research, and for theoretical conceptions of great fertility ; but it is now time to apply them to inorganic substances, and to see whether they are generally valid. Whatever result is reached, organic chemistry itself will be the gainer ; enriched by new suggestions and resting upon firmer foundations, its future advancement can be made all the more certain. Meanwhile, carbon compounds, by virtue of their serial relations, are of peculiar value in certain lines of physico-chemical investigations ; and they may also be profitably studied along the vague boundary which separates organic from inorganic chemistry. What we may call the contact phenomena between any two departments of knowledge are always interesting.

In the present revival of inorganic chemistry, a limited number of subjects have received the most attention. Among these I may name the study of double salts, of the rare earths, and of complex acids and bases. All this work is of value ; some of it is fundamental ; but more urgent, probably, is a revision of the older data concerning much simpler bodies. This task is not attractive ; it is far from brilliant in character and promises no startling discoveries ; but it is none the less essential if we wish to establish the foundations of chemistry more securely. Consider any group of inorganic compounds, as, for example, the anhydrous metallic halides, and we soon find that our knowledge of them is full of gaps, and that the descriptions of many presumably well-known substances are wretchedly incomplete and defective. To remedy this condition of affairs is no small matter ; there are errors to eliminate and careless work to be done over ; but with modern resources a great improvement is possible. Now, thanks to physical chemistry, we can determine molecular weights, either by cryoscopic or ebullioscopic methods ; and in the periodic law we have a basis for scientific classification. With these acids to research the new data should assume a theoretical value which formerly was lacking. For instance, the structural side of inorganic chemistry has been woefully defective ; but now, knowing the molecular weights of substances, problems of structure may be attacked to advantage. The conception of valency can also be tested to the uttermost degree.

Underlying all work upon compounds, however, is the study

of the elements themselves. We may speculate as to their ultimate nature, or we may condemn speculation as useless; but we must agree that accurate knowledge of their relations and properties is most desirable, and especially so with respect to physico-chemical researches. In order to correlate the properties of compounds with the properties of their components, we must first determine the latter, and our present knowledge in this direction is exceedingly incomplete. Not one element is thoroughly known on the physical side, and some, indeed, have not as yet been definitely isolated. What we require is the exact measurement of all the physical properties of all the chemical elements at all available temperatures; from such data laws are sure to follow. Here again the periodic law can guide us, for in its curves the measured constants are easiest compared. In this scheme, evidently the accurate determination of atomic weights is an important feature, for with them all else is coordinated. We also need to know, more completely than we do at present, the molecular weights of the free elements, because the reactions which we really observe are between molecules and not between atoms. Thus, when monatomic mercury unites with octatomic sulphur, the phenomena which occur involve the breaking-down of the sulphur molecule. If, instead of mercury, we have diatomic oxygen or tetratomic arsenic, the reaction with sulphur becomes still more complex, for in each case, before combination, two molecules must be dissociated. The dissociation, of course, implies a loss of energy, of unknown amount; and in thermochemical discussions this undetermined factor is the chief obstacle to progress. If we could study reactions between monatomic molecules alone, we should have ideally the simplest conditions for thermochemical measurement. But such reactions might be difficult to identify, if indeed, they are possible at all. These considerations are obvious enough, but, unfortunately, they are sometimes overlooked.

Of the second great problem of chemistry, the nature of chemical combination, I need say little more. Some of the subordinate questions which grow out of it have already been mentioned, and each of them is a center of activity in the chemical research of the day. The entire field, however, is not covered, and here and there we can see evidences of neglect. First, we need to know under what conditions chemical change is possible. Then, if we

would truly understand what chemical attraction means, we must study much more fully than hitherto its relations to other forces. How do heat, light, and electricity inaugurate a reaction, and how are they produced by it? Questions of equilibrium are important, but they are subordinate to these. Furthermore, is chemical union of one kind only, or do we confuse different phenomena under the single name? Some authors write of atomic and molecular combinations as if they were distinct; are they really so, or is the separation nothing more than a confession of ignorance? For example, what is water of crystallization? Here is one of the commonest phenomena of chemistry entirely unexplained.

Up to this point I have considered the needs of chemistry from the theoretical side alone, as if we had only a matter of pure science to deal with. But the question has other aspects, of equal importance to us, and these now claim our attention. In order to enlarge the possibilities of research, what more do we need in the way of opportunities and resources?

To the sporadic, the piecemeal, the almost accidental character of scientific investigation I have already referred. Rarely do we find a man who can take up a large problem in a large way, with all of its ramifications and details; even the most favored investigator must confine his personal work within narrow bounds, and do the best he can in his own corner. The greater part of chemical discovery has been the result of individual effort,—the work of men who labored independently of one another, with rare cooperation, and often under conditions of the least favorable kind. By an army of volunteers, undisciplined and unofficered, the victories of science have been won. The time is now ripe for something better: how to organize research is the problem to be solved.

I do not mean to imply, by this suggestion, that any existing agency for research should be destroyed, or even supplanted, for such a proposition would be foolish in the extreme. Individual initiative, personal enthusiasm, are too precious to be lost; they have their part to play in the development of science, and the smallest fact, discovered by the humblest worker, will always be welcome. I do believe, however, that present conditions may be improved; that the efficiency of the individual can be increased; and to this end I urge upon your consideration the possibility of

cooperation between those investigators who happen to be laboring in the same field. Ten men, pulling together, can do more than twenty who are apart. Duplication of effort, the useless repetition of work, can at least be avoided.

On several former occasions I have advocated, as the most urgent need of science, the regular endowment of research. By this I do not mean the payment of salaries to men working at random, who shall each choose his own small problem and attack it in his own way. Such a procedure would increase facilities, no doubt, but it might prove to be wasteful in the end. I look rather to the establishment of institutions, wherein bodies of trained men should take up, systematically and thoroughly, the problems which are too large for individuals to handle. Suppose that some of the wealth which chemistry has created, should return to it in the form of a well-built, well-equipped, and well-endowed laboratory, devoted to research alone;—what might we not expect from such a foundation! Libraries, museums, schools, and universities receive endowments by the score; observatories are equipped for astronomical research; why should not chemistry come in for her share of the benefactions? Are our achievements so great that we seem to need no aid? In this hint there is a modicum of truth; the users of chemistry, the great industrial leaders, see the wonderful resources of our science, and do not realize that she can require more. That the giver of help should herself demand assistance, is a hard thing to explain.

This, then, is our greatest need: the endowment of laboratories for systematic research, wherein chemistry and physics shall find joint provision. I say "systematic research," in order to distinguish it from the uncorrelated work of separate individuals. In physics, or for physics primarily, a beginning has already been made; the Reichsanstalt at Berlin, the new physical laboratory in London, and the Bureau of Standards at Washington, may cover a part of the ground. But it is only a part, for in each case, and in other like institutions, the researches are undertaken mainly in response to industrial demands; to furnish methods and standards rather than to develop principles and laws. The advancement of science as science is quite another affair. Neither does the Davy-Faraday Laboratory in London exactly meet our requirements. It is organized to help individuals, by giving facilities for work, but it does not provide for the systematic in-



vestigation of large problems, through the combined efforts of a body of chemists operating under a common plan. These institutions are all steps in the evolution of the research laboratory, but the development, as yet, is incomplete. Laboratories for instruction have been lavishly provided, but in them research is subordinate to teaching. The thesis of the student may represent good work; the leisure of the instructor may be fruitful also; but organized research is a different thing, and must have its own independent resources.

Either at public expense, or by private enterprise, laboratories for research should be established in all of the larger civilized countries. By conference between them their work could be so adjusted as to avoid repetition, each one reinforcing the others. Their primary function should be to perform the drudgery of science; to undertake the tedious, laborious, elaborate investigations from which the solitary worker shrinks, but which are nevertheless essential to the healthy development of chemistry. Brilliant discoveries might be made in them, but incidentally, and not as their main purpose. Such discoveries would surely follow if the fundamental work was well done, but the latter should come first as being the most essential. Whether we serve pure science or applied science, we all feel the need of data which are as yet undetermined, and whose ascertainment we cannot undertake ourselves. How often we are baffled in our own researches for want of just such material! In the verification of methods and the determination of constants, the research laboratory would have plenty to do, even were nothing more attempted.

By the creation of laboratories such as I have suggested, the independent scholar might be aided in many ways. The antecedent data, without which his researches are crippled, could often be furnished, thus opening pathways where obstacles now exist. Furthermore, the desirable cooperation between investigators would become a much simpler matter to arrange than it is now. Every laboratory for research would become a nucleus around which individual enterprises might cluster, each giving and receiving help. A great work, wisely planned, always attracts co-laborers; its mere suggestiveness is enough to provoke widespread intellectual activity. Here there is no monopoly, no limit to competition, no harmful rivalry; every research is the seed of other researches, and every advance made by one scholar implies

the advance of all. In the realm of thought we gain by giving, and the more lavish our offerings, the richer we become.

We glory in the achievements of chemistry, and we find merit also in its imperfections, for they give us something more to do. Never can the work be finished; never can all its possibilities be known. Hitherto the science has grown slowly and irregularly, testing its strength from step to step, and securing a sure foothold in the world. Now comes the time for better things: for system, for organization, for transforming the art of investigation itself into something like a science. The endowment of research is near at hand, and the results of it will exceed our most sanguine anticipations.

---

### A TYPE OF REACTION BY WHICH SODIUM CARBONATE AND HYDROCHLORIC ACID MAY BE FORMED IN THE ANIMAL ORGANISM.

BY THOMAS B. OSBORNE.

Received September 26, 1901.

IN a preceding paper<sup>1</sup> I have called attention to the basic properties of protein substances and have shown that preparations of the crystalline globulin edestin, as usually obtained from the hemp seed, are mixtures of salts, chiefly chlorides and sulphates. The nature of this combined acid depends upon the salts present in the solution at the time of precipitation, the acid of the seed sufficing to enable some of each of the acids of these salts to combine with the protein.

These facts led me to examine the precipitate produced by carbonic acid, in a dilute sodium chloride solution of edestin, as it seemed possible that this might consist chiefly of chloride.

A quantity of a relatively pure preparation of edestin, which had been several times recrystallized from a warm dilute sodium chloride solution by cooling, was suspended in water and made exactly neutral to phenolphthalein by decinormal potassium hydroxide solution. The edestin thus neutralized was washed with water and dissolved in sodium chloride brine. The solution was diluted with water until it became slightly turbid and carbonic acid gas was passed through it until the edestin appeared to be completely precipitated. This was filtered out, washed thoroughly with 1 per cent. sodium chloride solution

<sup>1</sup> This Journal, 24, 39.

and then with 50 per cent. alcohol, until no chlorine could be detected in the washings, dehydrated with absolute alcohol and dried over sulphuric acid. The substance thus prepared, while insoluble in dilute sodium chloride solution, was largely soluble in pure water, as well as in strong sodium chloride brine, yielding solutions acid to litmus and to phenolphthalein; to neutralize 1 gram to the latter indicator, 1.9 cc. of decinormal potassium hydroxide solution was required. Fifteen grams of this preparation were treated with freshly boiled water and 28.5 cc. of decinormal potassium hydroxide solution, diluted with much water, were added. The edestin, which separated completely from the solution, was then filtered out, washed with water and the filtrate and washings evaporated on a water-bath. The residue was dried at  $110^{\circ}$  and analyzed with the following results:

	Gram.
Organic matter.....	0.0222
Inorganic matter.....	0.2123
Total residue.....	0.2345

The inorganic residue contained :

	Gram.
Potassium chloride.....	0.1994
Potassium sulphate.....	0.0153

The potassium added was equivalent to 0.2127 gram of potassium chloride, so that over 93 per cent. of the potassium added was recovered as chloride. From this analysis we find that with 15 grams of edestin, equal to 13.5 grams dried at  $110^{\circ}$ , 0.0976 gram of hydrochloric acid or 0.072 per cent. of the protein had been precipitated. Corresponding to this quantity of hydrochloric acid, 0.1417 gram of sodium carbonate must have been produced in the salt solution by the carbonic acid. It seems probable that by a similar reaction both sodium carbonate and hydrochloric acid may be formed from sodium chloride in the organism, since there is always sodium chloride and protein matter present where carbonic acid is produced in the tissues.<sup>1</sup>

<sup>1</sup> Cf. Schulz: *Pflüger's Archiv.*, 27, 454.

## SULPHUR IN PROTEIN BODIES.

By THOMAS B. OSBORNE.

Received September 26, 1901.

### I. HISTORICAL

KRÜGER<sup>1</sup> has pointed out that the "sulphur content of legumin, casein, fibrin and ovalbumin are to each other as 4:8:12:16, from which one can conclude that the number of sulphur atoms in them are as  $1_n:2_n:3_n$ " \* \* \* "Leaving out of consideration the unknown molecular weight and, instead, taking into account the number of sulphur atoms, an equally great molecular weight may be assumed for all proteins. A comparison of this equally great atomic complex is possible, in respect to sulphur, because the proportion of the other elements in these bodies varies so little that it has no influence on the sulphur content."

Some time ago, before I was aware of Krüger's suggestions, I reached the same conclusion by a different line of reasoning. I pointed out<sup>2</sup> that the molecular weight of those proteins which contain but 0.4 per cent. of sulphur must be at least 15,000 if there are two atoms of sulphur in their molecules and that similar molecular weights are obtained for a large number of the more carefully analyzed proteins, if their simplest empirical formulas, calculated on the basis of a single atom of sulphur, are multiplied by such a whole number as to give molecular weights nearest to 15,000.

The results thus obtained all fall so near to one another as to strongly suggest that all these bodies have similar molecular weights not far from (15,000)<sub>n</sub>.

The fact that the proteins all react with very small quantities of acids and alkalies and closely resemble one another in many of their physical characters, also indicates that they have similar high molecular weights. Further, the oxyhemoglobins from horse and dog blood must contain at least one molecule of protein; and as these have been shown by Zinoffsky<sup>3</sup> and Jaquet<sup>4</sup> to contain, respectively, 2 and 3 atoms of sulphur to 1 of iron (see page 161), the protein contained in them cannot have a

<sup>1</sup> Krüger: *Pflüger's Archiv.*, 43, 244.

<sup>2</sup> *This Journal*, 21, 486.

<sup>3</sup> *Ztschr. Physiol. Chem.*, 10, 16.

<sup>4</sup> *Ibid.*, 12, 284, and 14, 289.

molecular weight very far from 15,000, or a multiple of this. Furthermore, Sabanieff,<sup>1</sup> in studying the lowering of the freezing-point caused by colloid substances, found that those colloids, of which the molecular weight was known, depressed the freezing-point to nearly the calculated extent and that the depression of the freezing-point caused by purified ovalbumin indicated a molecular weight of about 15,000, a result which shows that the molecular weight of this substance is, at least, much higher than that corresponding to three atoms of sulphur.

In view of these considerations it seemed important to determine, as accurately as possible, the total sulphur in a considerable number of different proteins, in order to learn whether this formed a perfectly definite constituent of these substances and to also determine whether the fraction of this sulphur, converted into sulphide by heating with strong alkaline solutions, corresponded to a definite number of the atoms in the formulas calculated according to the method above described.

Fleitmann<sup>2</sup> long ago showed that a part only of the sulphur of proteins was removed by heating with caustic alkali. Danielewski<sup>3</sup> confirmed Fleitmann's observations and later<sup>4</sup> called attention to their importance and to the fact that they had apparently been disregarded by all those writers who had attempted to give formulas for the protein bodies, since these formulas were all constructed on the basis of a single sulphur atom.

Krüger<sup>5</sup> determined the proportion of sulphur thus detached from ovalbumin and from fibrin and discussed at length the possible ways in which this sulphur could be united within the atomic complex which was split off and also the way in which the remaining sulphur could be united within the protein molecule. He also gave a table showing the structural formulas of various well-known sulphur compounds and, as far as possible, the behavior of these toward alkaline lead solutions.

Suter<sup>6</sup> studied the behavior of several proteins when treated with hot alkaline lead solutions, and noted, as did Krüger before him, the similarity of their behavior to that of cystin under the same conditions.

<sup>1</sup> *Chem. Centrbl.*, 10, 1891.

<sup>2</sup> Fleitmann: *Ann. Chem.* (Liebig), 61, 121, and 66, 380 (1847).

<sup>3</sup> Danielewski: *Ztschr. Chem.*, 12, 41 (1869).

<sup>4</sup> Danielewski: *Ztschr. physiol. Chem.*, 7, 443 (1883).

<sup>5</sup> Krüger: *Pflüger's Archiv.*, 43, 244 (1888).

<sup>6</sup> Suter: *Ztschr. physiol. Chem.*, 20, 564 (1895).

Schulz<sup>1</sup> reviewed the work of the preceding investigators and attributed the lack of agreement between their quantitative results to a partial oxidation of the sulphide during the long heating required for its complete separation. This he attempted to obviate by adding metallic zinc to the soda solution. After satisfactorily testing this method with sodium thiosulphate, sulpho-urea, and thioacetic acid, he applied it to several proteins.

Since the work to be described in this paper was completed, K. A. H. Moerner<sup>2</sup> has isolated cystin from the decomposition products of horn, hair, egg membrane, and serum albumin and further found that in the solutions freed from cystin another sulphur-containing body was present which yielded lead sulphide on treatment with hot alkaline lead solutions. This latter body, however, he did not identify. Embden<sup>3</sup> has independently confirmed Moerner's observations, but considers cystein to be the primary decomposition product of serum and egg albumin and of edestin, and that cystin is a secondary product derived from cystein.

Since Schulz's method appears to yield satisfactory results, I have used it to determine the amount of loosely bound sulphur in a number of the protein substances which have been prepared and studied during the past few years in this laboratory and have compared the results with those obtained by heating the proteins under pressure with strong alkaline solutions at various temperatures. I have also carefully determined the total sulphur which these proteins contain, and give the amount found in each, in the following pages.

## II. ANALYTICAL METHODS.

### *a. Determination of Total Sulphur.*

About 10 grams of sodium peroxide were converted into hydroxide<sup>4</sup> in a nickel crucible by adding a little water and boiling over an alcohol lamp until the excess of water was expelled. From 1 to 2 grams of the protein were then stirred into the slightly cooled hydroxide and oxidized by gradually raising the heat and adding small portions of sodium peroxide until the oxidation was

<sup>1</sup> Schulz: *Ztschr. physiol. Chem.*, 25, 16 (1898).

<sup>2</sup> Moerner: *Ibid.*, 28, 595 (1899); also *Proceed. 13th Inter. Con. Med. Sec. d. physiol.*, etc., p. 15, Paris, 1900.

<sup>3</sup> Embden: *Ztschr. physiol. Chem.*, 32, 94 (1901).

<sup>4</sup> I have found commercial sodium peroxide to be freer from sulphur than most preparations of so-called chemically pure sodium hydroxide made from the metal, and as the former is very much cheaper than the latter it is advantageous to use it as here described.

complete. The fused mass was then dissolved in 400 cc. of water, its solution strongly acidified with hydrochloric acid, boiled until the excess of peroxide was destroyed and chlorine expelled, filtered through pure paper, made neutral with ammonia, and an excess of 4 cc. of concentrated hydrochloric acid added. From the boiling solution, sulphuric acid was precipitated by gradually adding a solution containing 1 gram of barium chloride. After standing over night on a steam table, the barium sulphate was filtered out, washed, ignited, and weighed.

*b. Determination of Loosely Bound Sulphur—Schulz's Method.*

Schulz's method consists in boiling, with a reflex condenser for several hours, 1 gram of the protein with 50 cc. of 30 per cent. sodium hydroxide solution containing 1 gram of metallic zinc and a little lead acetate. After slightly acidifying the solution with acetic acid, the lead sulphide formed is filtered out, washed with water, dried and fused, together with the filter-paper, with sodium hydroxide and potassium nitrate. In following Schulz's method, the lead sulphide was fused with sodium hydroxide and peroxide. The fusion is dissolved in water, its solution treated with carbonic acid (to remove lead), filtered, evaporated with an excess of hydrochloric acid, and sulphur determined as barium sulphate in the usual way.

*Pressure Method.*

From 1 to 5 grams of the protein were thoroughly mixed in a nickel crucible with 50 cc. of 50 per cent. sodium hydroxide solution containing some lead acetate, and the mixture heated in an autoclave for from two to seven hours, at temperatures of from 135° to 165° C., oxidation being prevented by absorbing the oxygen in the air within the autoclave with sodium pyrogallate. The lead sulphide, formed by thus heating, was filtered out, washed with water, dried, fused with sodium hydroxide and peroxide, and since the presence of silica was avoided by using nickel vessels, the sulphur was precipitated as barium sulphate directly from the acidified solutions of the fusion under the conditions used for determining total sulphur.

III. DETERMINATION OF TOTAL AND LOOSELY BOUND SULPHUR IN VARIOUS PROTEINS.

*Edestin.*

This protein occurs in the seeds of hemp, flax, and squash, and

also in the castor bean. As edestin separates readily in octahedral crystals when its saline solutions are dialyzed or cooled, relatively pure preparations of it can easily be made.

In order to learn with what degree of accuracy the total sulphur can be estimated and to establish the constancy of its sulphur content I have made the following determinations in twenty-four different crystallized preparations from the hemp seed, representing numerous fractional precipitations and different methods of preparation.

TABLE I.—PERCENTAGE OF TOTAL SULPHUR IN PREPARATIONS OF EDESTIN FROM HEMP SEED.

I.	II.	III.	IV.	V.	VI.	VII.
0.931	0.934	0.980	0.895	0.983	0.960	0.944
0.942	0.924	0.938	....	0.963	....	0.941
0.910	0.937	....	....	....	....	....
VIII.	IX.	X.	XI.	XII.	XIII.	XIV.
0.990	0.990	0.997	0.943	0.874	0.864	0.900
0.972	....	0.987	....	0.900	0.866	....
0.963	....	....	....	....	....	....
XV.	XVI.	XVII.	XVIII.	XIX.	XX.	XXI.
0.902	0.893	0.934	0.941	0.964	0.939	0.932

The average of these figures is 0.936 per cent., the lowest being 0.066 per cent. below, the highest 0.06 per cent. above the average. The difference shown by these several preparations are not analytical, as the extreme figures are confirmed by closely agreeing duplicates.

It is evident from these results that it is possible to determine total sulphur with considerable accuracy, and it is also evident that these several preparations do not contain exactly the same amount of sulphur. I have previously shown<sup>1</sup> that, owing to the natural acidity of the seed, crystallized edestin, as usually prepared, consists of a mixture of compounds of a basic protein molecule with acids, the nature of the acids depending upon the character and proportion of the salts present at the time the edestin was precipitated. Thus, when preparation XXIII, crystallized from ammonium sulphate solution, was suspended in water and neutralized to phenolphthalein by potassium hydroxide solution, the edestin remained undissolved and was separated by filtration from the water, in which was found a quantity of potassium sulphate corresponding to the amount of acid neutralized. This and another preparation similarly made contained the following amount of total sulphur :

<sup>1</sup> This Journal, 24, 39.



	XXII. Per cent.	XXIII. Per cent.
Sulphur {	1.125	1.084
	1.110	
	1.103	

The acidity of these preparations to phenolphthalein was equal to an amount of sulphuric acid corresponding to the excess of sulphur in them above that of the average of I-XXI, all of which latter were made from sodium chloride solutions. These latter preparations, neutralized in the above described manner, yielded chiefly potassium chloride, but together with this chloride a small proportion of sulphate was always found. The differences in sulphur content of preparations I-XXI are thus explained. This excess of sulphur is therefore not to be regarded as belonging to the protein molecule. The amount of such sulphur is not great, since the total acidity of the preparations in no case exceeded 1.2 cc. of a decinormal solution per gram, which corresponds to sulphuric acid containing sulphur equivalent to 0.19 per cent. of the protein.

Such an excess of sulphur is shown by preparations XXII and XXIII in which, as already stated, I found by actual analysis that the acidity was due to sulphuric acid.

In order to find the true amount of sulphur belonging to the edestin molecule I determined the total sulphur in a very pure and perfectly neutral preparation, made by several times recrystallizing edestin chloride, neutralizing its solution to phenolphthalein and again crystallizing. Two determinations of sulphur in this preparation gave 0.880 and 0.887.

The average of these figures, 0.884, unquestionably closely represents the total sulphur contained in the edestin *molecule*.

With this result several of the preceding agree closely (namely, IV, XII, XIII, XIV, XV, and XVI), all of which are either preparations consisting mostly of bichloride, soluble in pure water, which neutralization experiments have shown to yield extremely small amounts of potassium sulphate, or were preparations obtained from solutions made neutral to phenolphthalein.<sup>1</sup>

In order to learn with how much accuracy the loosely bound sulphur of edestin can be determined, the following large number of trials were made :

<sup>1</sup> This Journal, 24, 39.

TABLE II.—PERCENTAGE OF LOOSELY BOUND SULPHUR IN EDESTIN.

One gram boiled with 30 per cent. NaOH, Zn, and $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$ . 7½ hours.					
VIII.	XI.	XVI.	XVII.	XXIII.	XX.
0.282	0.376	0.355	0.309	0.297	0.348
0.263	0.286	0.321	0.303	....	0.302
....	0.277	0.277	....	....	....
....	....	....	....	....	....
One gram heated in autoclave with 30 per cent. NaOH and $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$ . 5 grams at 165°.					
At 135°, 2 hours.		At 135°, 3 hours.			7½ hours.
VIII.	XXIII.	VIII.	XVI.	XXIII.	XXIV.
0.366	0.307	0.276	0.275	0.314	0.339
0.297	....	....	0.265	0.300	0.344
....	....	....	....	0.297	....
....	....	....	....	0.240	0.340
					0.337

Of the determinations made with 1 gram of edestin, four are as high as those obtained with 5 grams at the higher temperature ; the average of them all, however, is slightly but distinctly lower. As the results obtained with 5 grams of edestin at the higher temperature are probably the most accurate, their average, 0.346 per cent., may be considered to most closely represent the proportion of loosely bound sulphur, which can be obtained from edestin as lead sulphide.

### Excelsin

Excelsin is obtained from the Brazil-nut (*Bertholletia excelsa*) by extraction with sodium chloride brine and is deposited in crystalline hexagonal plates by dialyzing its saline solutions. Five different preparations of excelsin contained the following amounts of sulphur :

TABLE III.—PERCENTAGE OF TOTAL SULPHUR IN EXCELSIN.

1. <sup>1</sup>	2. <sup>1</sup>	3. <sup>1</sup>	4. <sup>2</sup>	5. <sup>2</sup>
1.06	1.12	1.07	1.083	1.109

The average of these figures, 1.088, closely represents the total sulphur of excelsin.

In making preparation 4, the oil-free meal was extracted with sodium chloride brine, the extract saturated with ammonium sulphate, the precipitate produced dissolved in water, its solution made neutral to litmus with sodium carbonate, and the excelsin precipitated in crystals by dialysis in water.

<sup>1</sup> Osborne : *Am. Chem. J.*, 14, 662.

<sup>2</sup> Preparations made recently.

Preparation 5 was made by dialyzing a perfectly clear sodium chloride extract of the oil-free meal in running water, whereby the excelsin was deposited in uniformly large hexagonal plates.

As no more sulphur was found in preparation 4 than in 5, it is evident that excelsin does not take up sulphuric acid from its saline solutions as readily as edestin does.

Excelsin is soluble in water when made neutral to phenolphthalein and therefore it has not been possible to identify the acids which are combined with it by the method applied to edestin.

The amount of loosely bound sulphur was determined in preparations 4 and 5 under the conditions given below.

TABLE IV.—PERCENTAGE OF LOOSELY BOUND SULPHUR IN EXCELSIN.

One gram boiled with 30 per cent. NaOH, Zn, and Pb(C <sub>2</sub> H <sub>3</sub> O <sub>2</sub> ) <sub>2</sub> . 7½ hours.		Heated in autoclave with 30 per cent. NaOH.		
4	5	4	One gram at 135° 2 hours. 5	Five grams at 165° 4½ hours. 5
0.339	0.347	0.294	0.293	0.350
0.321	0.344	....	....	....
0.289	0.297	....	....	....
0.277	0.290	....	....	....
0.257	0.284	....	....	....
....	0.281	....	....	....

The result obtained at 165° agrees closely with the higher figures found by Schulz's method, and as experimental errors were diminished in this determination by employing a larger amount of substance, 0.350 per cent. may be taken as the proportion of loosely bound sulphur that can be obtained from excelsin.

### *Legumin.*

Legumin, found in considerable quantity in the seeds of the pea, horse bean, vetch and lentil, is a protein substance having the properties of a globulin. It is not a nucleo-proteid, as stated by Hammarsten, since the many pure preparations, which I have made, were entirely free from phosphorus.<sup>1</sup> The loosely bound sulphur was determined in carefully purified preparations, made according to the methods described in my papers last cited. Several closely agreeing new determinations of the total sulphur in these preparations showed them to contain the following proportion :

<sup>1</sup> Osborne : Report of the Connecticut Agricultural Experiment Station for 1895, p. 262, and 1897, p. 324; also This Journal, 18, 583, and 20, 348, 362, 393, 406, and 410.

TABLE V.—PERCENTAGE OF TOTAL SULPHUR IN LEGUMIN.

Pea.	Lentil.	Horse-bean.	Vetch.
0.371	0.390	0.390	0.389

The percentage of loosely bound sulphur obtained from these preparations by different methods was as follows :

TABLE VI.—PERCENTAGE OF LOOSELY BOUND SULPHUR IN LEGUMIN.

	One gram boiled with 30 per cent. NaOH, Zn, and $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$ , 7½ hours.	One gram with 30 per cent. NaOH and $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$ at 135°. 2 hours.	Five grams with 30 per cent. NaOH, Zn, and $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$ at 165°. 5 hours.
Pea .....	{ 0.143 0.143	....	....
Horse-bean ....	0.193	0.164	0.186
Lentil .....	0.193	....	....
Vetch .....	{ 0.159 0.160	....	0.150

The average of the figures for total sulphur is 0.385 per cent. and for the loosely bound sulphur 0.166 per cent.

### *Vignin.*

Under this name I described the chief protein of the cow pea<sup>1</sup> and gave its sulphur content as 0.50 per cent.

Through an oversight, the correction for a small amount of sulphur contained in the reagents used at that time was omitted and consequently this figure for sulphur is a little too high. I have since repeated these determinations on all but one of the preparations described, and have obtained the following results :

TABLE VII.—PERCENTAGE OF TOTAL SULPHUR IN VIGNIN.

	1	2	3	4	6	8	9
S.....	0.382	0.443 0.439	0.356	0.365	0.360	0.416	0.417

The average of these figures is 0.391.

Preparation 2 constituted the greater part of all the protein extracted from the seed, whereas 3, 4, and 6, successively precipitated from the filtrate from 2, formed a relatively small part of the total protein matter. As 8 and 9, fractions of 2, contain nearly the same quantity of sulphur as 2, the average of the figures given for these three preparations, 0.426, may be taken as closely representing the total sulphur or vignin.

<sup>1</sup> Report of Connecticut Agricultural Experiment Station for 1896, p. 380; also *This Journal*, 19, 494.

TABLE VIII.—PERCENTAGE OF LOOSELY BOUND SULPHUR IN VIGNIN.

One gram boiled with 30 per cent. NaOH, Zn, and $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$ . 7½ hours.	One gram with 30 per cent. NaOH and $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$ at 135°. 3 hours.
0.210	0.220
0.213	....

The average of these figures is 0.214 per cent.

### *Amandin.*

Amandin is the most abundant protein in the seeds of the almond and peach.

In a former paper<sup>1</sup> I gave the total sulphur in five preparations of amandin as follows :

TABLE IX.—PERCENTAGE OF TOTAL SULPHUR IN AMANDIN.

1	2	3	4	5
0.39	0.44	0.48	0.45	0.48

A redetermination of sulphur in 3, using 1.6688 grams, gave 0.429 per cent. Preparations 2, 3, and 4 were precipitated with ammonium sulphate; 1 and 5 were made without using this salt.

The recent determination of sulphur, which is probably the most accurate, shows that amandin contains about 0.429 per cent. of sulphur.

TABLE X.—PERCENTAGE OF LOOSELY BOUND SULPHUR IN AMANDIN.

One gram boiled with 30 per cent. NaOH, Zn, and $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$ at 135°. 2 hours.	Five grams with 30 per cent. NaOH and $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$ at 165°. 3 hours.
0.180	0.217
0.172	....
0.165	....

The result obtained at the higher temperature and with the larger amount of substance is doubtless the most correct of the above figures, so that 0.217 per cent. may be taken as the proportion of sulphur which can be obtained from amandin, as sulphide.

### *Glycinin.*

The greater part of the protein matter of the soy bean is glycinin, a globulin described in a paper previously published.<sup>2</sup> Careful redeterminations of sulphur in several of the preparations, described in the paper cited, showed that the figures there given were nearly correct; the average of the new determinations gave

<sup>1</sup> Osborne and Campbell: Report of the Connecticut Agricultural Experiment Station for 1895; This Journal, 18, 487.

<sup>2</sup> Osborne and Campbell: Report of the Connecticut Agricultural Experiment Station for 1897; also This Journal, 20, 419.

0.700 per cent. of sulphur against the published figure, 0.72 per cent. The total sulphur in glycinin is therefore 0.710 per cent.

TABLE XI.—PERCENTAGE OF LOOSELY BOUND SULPHUR IN GLYCININ.

	One gram boiled with 30 per cent. NaOH, Zn, and $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$ , 7½ hours.	Five grams with 30 per cent. NaOH and $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$ at 165°, 3 hours.
	0.321	0.317
Preparation 2 . . . . .	0.305	....
	0.274	....
	0.263	....
Preparation 14 . . . . .	0.286	....

Since the result obtained with 5 grams of glycinin agrees closely with the higher figures obtained by boiling at the atmospheric pressure, we may safely assume that glycinin yields very nearly 0.320 per cent. of sulphur as sulphide.

#### *Gliadin.*

Gliadin, soluble in alcohol of 70–80 per cent., is one of the most abundant proteins of the wheat kernel. In a paper on the protein constituents of this seed,<sup>1</sup> the total sulphur of gliadin was given as 1.14 per cent.

This figure was the average found in a large number of preparations, all of which were not entirely pure. Careful redeterminations of sulphur in several of the purest of these preparations gave the following results :

TABLE XII.—TOTAL SULPHUR IN GLIADIN.

17	23	28	29	33
1.124	1.002	1.022	1.030	1.058
1.124	....	1.005	....	1.027

Excluding the figures given for 17, which for some reason contains more sulphur than the others, the average sulphur content of gliadin appears to be 1.027 per cent.

The preparation of gliadin used in the following experiments consisted of a mixture of several of the purer products obtained in the former investigation and contained 1.044 per cent. of sulphur.

TABLE XIII.—PERCENTAGE OF LOOSELY BOUND SULPHUR IN GLIADIN.

One gram boiled with 30 per cent. NaOH, Zn, and $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$ , 7½ hours.	One gram with 30 per cent. NaOH and $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$ at 135°, 4 hours.	Five grams with 30 per cent. NaOH and $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$ at 165°, 5 hours.
0.627	0.635	0.624
0.516	....	0.611
....	....	0.600

<sup>1</sup> Osborne and Voorhees: *Am. Chem. J.*, 18, 392.

The average of these figures, excluding the lowest, is 0.619, which doubtless nearly represents the percentage of loosely bound sulphur in gliadin.

### *Hordein.*

Hordein, soluble in strong alcohol, occurs in quantity in the barley grain.

In ten different preparations, representing fractional precipitations of this substance, the average content of sulphur was 0.83 per cent.<sup>1</sup> In a preparation recently made for the experiments here described, the total sulphur was 0.847 per cent.

TABLE XIV.—PERCENTAGE OF LOOSELY BOUND SULPHUR IN HORDEIN.

One gram boiled with 30 per cent. NaOH, Zn, and $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$ , 7½ hours.	One gram with 30 per cent. NaOH and $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$ at 135°, 4 hours.	Five grams with 30 per cent. NaOH and $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$ at 165°, 3 hours.
0.348	0.338	0.358

The average of these figures gives 0.348 per cent. of loosely bound sulphur in hordein.

### *Zein.*

Zein is the most abundant protein found in the maize kernel. It is especially characterized by its ready solubility in alcohol of 90 to 95 per cent., though in absolute alcohol it is wholly insoluble. In a former paper<sup>2</sup> the average amount of total sulphur, in nine different preparations of zein, was given as 0.60 per cent.

TABLE XV.—PERCENTAGE OF LOOSELY BOUND SULPHUR IN ZEIN.

One gram boiled with 30 per cent. NaOH, Zn, and $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$ , 7½ hours.	One gram with 30 per cent. NaOH and $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$ at 135°, 2 hours.	Five grams with 30 per cent. NaOH and $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$ at 165°, 4½ hours.
0.243	0.161	0.212
0.248	0.160	....

The result obtained with five grams of zein at 165° probably represents most nearly the amount of loosely bound sulphur yielded by zein, which may therefore be taken as 0.212 per cent.

### *Phaseolin.*

In a former paper on the proteins of the kidney bean,<sup>3</sup> I gave the average amount of sulphur found in twenty-four different preparations of phaseolin as 0.56 per cent. Among these preparations

<sup>1</sup> Osborne: Report of the Connecticut Agricultural Experiment Station for 1894, p. 165; also This Journal, 17, 539.

<sup>2</sup> Chittenden and Osborne: *Am. Chem. J.*, 13, 327, 385, and 14, 20.

<sup>3</sup> Osborne: Report of the Connecticut Agricultural Experiment Station for 1893; also This Journal, 11, 16, 633, 703 and 757.

was one consisting almost wholly of octahedral crystals in which duplicate determinations give 0.33 and 0.29 per cent. of sulphur. I have since prepared a large quantity of phaseolin by extracting the bean meal with 10 per cent. ammonium sulphate solution, precipitating the proteins by saturating the extract with the same salt, dissolving the precipitate in water, filtering the resulting solution and then dialyzing it for four days. The precipitate which first formed consisted of relatively large octahedral crystals, with which amorphous matter was afterwards deposited. This precipitate, A<sub>1</sub>, was filtered out, redissolved in ammonium sulphate solution and the filtered liquid dialyzed for four days, whereupon considerable precipitate, A<sub>2</sub>, separated, consisting of amorphous matter and octahedral crystals, some of which were large enough to be easily recognized by the naked eye. Several grams of these crystals, A<sub>a</sub>, were separated by elutriation nearly free from amorphous matter and were found to contain 0.265 per cent. of sulphur. The solution filtered from this last dialysis precipitate yielded, after seven days' further dialysis, 58 grams of partly crystallized phaseolin, A<sub>1</sub>, which contained 0.328 per cent. of sulphur.

The filtrate from the first dialysis precipitate, A<sub>1</sub>, above described, after dialyzing for four days more, gave a large precipitate which, when redissolved and again precipitated by dialysis, yielded 67 grams of A<sub>2</sub>, containing 0.356 per cent. of sulphur. By dialyzing the filtrate from the first precipitation of A<sub>2</sub> for seven days longer, 22 grams of A<sub>3</sub> were obtained, which contained 0.417 per cent. of sulphur.

From these results and those of the earlier investigation, it appears that uncertainty still exists respecting the total sulphur of phaseolin, and until we can prepare this substance in a completely crystallized condition it is impossible to assign a precise value to its sulphur content.

TABLE XVI.—PERCENTAGE OF LOOSELY BOUND SULPHUR IN PHASEOLIN.

	One gram boiled with 30 per cent. NaOH, Zn, and Pb(C <sub>2</sub> H <sub>3</sub> O <sub>2</sub> ) <sub>2</sub> . 7½ hours.	Five grams with 30 per cent. NaOH and Pb(C <sub>2</sub> H <sub>3</sub> O <sub>2</sub> ) <sub>2</sub> at 165°. 5½ hours.
Preparation A <sub>1</sub> ....	{ 0.062 0.079	0.063
Preparation A <sub>2</sub> ....	{ 0.092 0.076	....

The average of these figures is 0.072 per cent.



*Vicilin.*

Vicilin is a globulin, found by the writer in the seeds of the pea, lentil, and horse bean, and described in papers published some time ago.<sup>1</sup> This substance, like phaseolin, presents an uncertainty respecting its total sulphur. Twenty-one preparations, whose complete analyses agreed closely in other respects, contained from 0.23 to 0.08 per cent. of sulphur. This difference was not analytical, as the extreme figures were confirmed by duplicate determinations; thus for preparation 62, I found 0.08 and 0.07 per cent., for 84 0.10 and 0.09, and for 94 0.103 and 0.099 per cent., while for 55 I obtained 0.21 and 0.24, and for 58 0.21 and 0.20 per cent. of sulphur.

This difference among the preparations might be due to a mixture of a sulphur-free protein and legumin, with which vicilin is associated in these seeds, but this seems hardly possible, since the preparations with 0.20 per cent. of sulphur would, in this case, contain 50 per cent., and those with 0.10 per cent. of sulphur 25 per cent. of legumin, which, if present in such different proportions, would probably cause greater differences in composition than were shown by the successive fractional precipitations of vicilin, which apart from sulphur showed no notable differences in composition. Further, the very limited solubility of legumin in the dilute salt solutions, from which vicilin was obtained, makes it highly improbable that we have here a mixture of a sulphur-free protein with a very notable amount of legumin.

The actual sulphur content of vicilin is a matter of importance in relation to the molecular weight of this substance, since, if but one atom of sulphur is contained in its molecule and sulphur is present in all the molecules of those preparations which contained but 0.10 per cent. of sulphur, the molecular weight of vicilin must be approximately 30,000 and if the molecules contain two atoms of sulphur, 60,000. It is possible, however, that the sulphur-containing complex in vicilin is so loosely combined that it is easily detached, so that the preparations become mixtures of molecules containing sulphur and those containing none. This latter possibility seems probable since 1.58 grams of 94, from the horse bean, in which two determinations gave 0.103 and 0.099 per cent. of total sulphur, when heated for three hours with 30

<sup>1</sup> Osborne and Campbell: Report of the Connecticut Agricultural Experiment Station for 1897; also this Journal, 20, 348, 362, 393, and 410.

per cent. sodium hydroxide and lead acetate at a temperature of  $165^{\circ}$ , yielded but a trace of lead sulphide. Unfortunately no more of any other preparation containing so little sulphur was available, with which this observation could be confirmed.

The amount of loosely bound sulphur found in vicilin was determined in a preparation from the pea which contained 0.220 per cent. of total sulphur.

TABLE XVII.—PERCENTAGE OF LOOSELY BOUND SULPHUR IN VICILIN.

One gram boiled with 30 per cent. NaOH, Zn, and $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$ , 7½ hours.	Five grams with 30 per cent. NaOH and $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$ at $165^{\circ}$ , 4½ hours.
0.117	0.084
0.087	....

Five grams of another preparation, 93, which contained 0.150 per cent. of total sulphur, when treated for four and one-half hours at  $165^{\circ}$  with 30 per cent. sodium hydroxide and lead acetate, yielded 0.058 per cent. of sulphur as sulphide.

From these results it seems possible that from vicilin, sulphur is more easily detached than from the other proteins.

#### *Conglutin.*

An extended study of conglutin has shown<sup>1</sup> that from the seeds of the yellow lupin, by extracting with brine and precipitating by dialysis or by abundant dilution, preparations are obtained which contain about 0.9 per cent. of sulphur, while from the blue lupin preparations similarly obtained contain from 0.40 to 0.50 per cent. By fractional precipitation the crude conglutin from the yellow lupin can be separated into fractions, which have a pretty constant sulphur content, the one containing from 0.5 to 0.6 per cent., the other 1.4 to 1.5 per cent. The preparations with the larger quantity of sulphur contain about 1.5 per cent. less carbon than those with the smaller and also a little more nitrogen. Fractional precipitation of crude conglutin from the blue lupin gives products differing little in composition though the more soluble contain somewhat less carbon and nitrogen and a very little more sulphur. In the less soluble fractions, which have otherwise nearly the same composition and properties, somewhat different amounts of sulphur were found; thus, four fractions contained: 37, 0.32; 39, 0.24; 42, 0.38; and 44, 0.33 per cent. Although these differ-

<sup>1</sup> Osborne and Campbell: Report of the Connecticut Agricultural Experiment Station for 1896, p. 288; also This Journal, 18, 609; also Ritthausen; *J. prakt. Chem.*, 103, 78; *Ibid.*, n. f., 24, 222, and 26, 422, and Elweisskörper, etc., Bonn, 1872.

ences are slight they were shown to be actual by recently repeated determinations, using large quantities of substance.

The average composition of the least soluble fractions from the blue and yellow lupin is very nearly the same with the exception of sulphur, about 0.2 per cent. more of which is found in the latter.

The preparations obtained from these two seeds appear to be either compounds of one and the same protein body, conglutin, with more or less of some substance rich in sulphur, which is present in greater amount in the yellow than in the blue lupin, or mixtures of various proportions of similar proteins which contain very different amounts of sulphur. This latter supposition appears the more probable because about the same *proportion* of loosely bound sulphur was found in all the preparations, whether they contained 0.3 per cent. or 1.4 per cent. of total sulphur. It is improbable that a sulphur-containing substance is combined with the protein from which the same proportion of lead sulphide can be obtained as from the protein itself.

The total sulphur in the different preparations of conglutin used in the following experiments was :

TABLE XVIII.—PERCENTAGE OF TOTAL SULPHUR IN DIFFERENT FRACTIONAL PRECIPITATES OF CONGLUTIN.

Blue lupin.		Yellow lupin.		
I	II	III	IV	V
0.393	0.359	0.530	0.954	1.378

TABLE XIX.—PERCENTAGE OF LOOSELY BOUND SULPHUR IN THE ABOVE PREPARATIONS.

One gram boiled with 30 per cent. NaOH, Zn, and Pb(C <sub>2</sub> H <sub>3</sub> O <sub>2</sub> ) <sub>2</sub> .		One gram with 30 per cent. NaOH and Pb(C <sub>2</sub> H <sub>3</sub> O <sub>2</sub> ) <sub>2</sub> at 165°.	
7½ hours.		5¼ hours.	
Preparation I	0.288	....	
	0.264	....	
	0.233	....	
Preparation II	0.239	....	
Preparation III	0.344	0.372	
Preparation IV	0.558	....	
Preparation V	0.889	....	

These figures show that very nearly two-thirds of the sulphur of each of these preparations was obtained as lead sulphide, the amounts found falling between 59 to 70 per cent. of the total sulphur.

*Oxyhemoglobin from Dog's Blood.*

Hoppe-Seyler<sup>1</sup> found 0.39 per cent. of sulphur in oxyhemoglobin from dog's blood. Jaquet<sup>2</sup> found 0.5417 and 0.5414 per cent. of sulphur in this substance and later<sup>3</sup> 0.5688 and 0.5665. Jaquet's determinations were made with very great care and a large amount of carefully recrystallized substance was used for each determination.

In two carefully prepared and repeatedly recrystallized preparations of this substance,<sup>4</sup> I have found 0.600 and 0.567 per cent., and in another preparation once recrystallized 0.546 per cent. of total sulphur.

The average of Jaquet's determinations and my own gives 0.5618 per cent. of total sulphur in dog's blood oxyhemoglobin.

Six grams of oxyhemoglobin, once recrystallized, when heated for seven and one-half hours at 165° with 30 per cent. sodium hydroxide and lead acetate, gave 0.342 per cent. of loosely bound sulphur, and five grams of another preparation which had been recrystallized several times gave, under the same conditions, 0.328 per cent. The average of these figures, 0.335 per cent., doubtless closely represents the proportion of loosely bound sulphur contained in this substance.

*Ovalbumin.*

In an investigation of the protein constituents of the egg white, the results of which have been recently published,<sup>5</sup> I determined, with special care, the total amount of sulphur contained in ovalbumin. In ten different preparations of repeatedly recrystallized ovalbumin I found the following quantities :

TABLE XX.—PERCENTAGE OF TOTAL SULPHUR IN OVALBUMIN.

A1.	A2.	H1.	H2.	B1.	B2.	C1.	C2.	No. 2.	No. 3.
1.610	1.612	1.572	1.644	1.613	1.619	1.613	1.634	1.590	1.651

The details of the methods employed for the production of these preparations and the evidence of their purity may be found in the paper cited under the designations given in the above table.

<sup>1</sup> Hoppe-Seyler : *Med. Untersuch.*, 1868, p. 370.

<sup>2</sup> Jaquet : *Ztschr. physiol. Chem.*, 12, 285.

<sup>3</sup> *Ibid.*, 14, 269.

<sup>4</sup> I am indebted to the kindness of Prof. L. B. Mendel for an abundant supply of this oxyhemoglobin from which the preparations used in these experiments were made.

<sup>5</sup> Report of the Connecticut Agricultural Experiment Station for 1899; also *This Journal*, 22, 422.

These figures agree well with those given by several other investigators, namely :

Hammarsten.....	1.64
Bondzynski and Zoya.....	1.66
Krüger.....	1.66
Hopkins.....	1.57

Taking the average of my figures as nearly correct, the total sulphur in ovalbumin may be given as 1.616 per cent.

TABLE XXI.—PERCENTAGE OF LOOSELY BOUND SULPHUR IN OVALBUMIN.

One gram boiled with 30 per cent. NaOH, Zn and $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$ , 7½ hours.	One gram with 30 per cent. NaOH and $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$ at 135°, 2 hours.	Five grams with 30 per cent. NaOH and $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$ at 165°, 4½ hours.
0.523	0.523	0.491
0.511	0.518	....
0.504	0.505	....
0.471	0.459	....
0.455	0.441	....
0.425	....	....

The result obtained with five grams at 165° agrees very closely with the average of the others and is also in accord with the results obtained by Krüger<sup>1</sup>, Malerba<sup>2</sup> and Schulz<sup>3</sup>, who found, respectively, 0.44, 0.49 and 0.49 per cent. of loosely bound sulphur in ovalbumin. The amount of sulphur that can be obtained as sulphide by treating ovalbumin with hot alkali is therefore 0.491 per cent.

#### *Ovovitellin.*

The substance used in these experiments was preparation 2 described in a former paper on the proteins of the egg yolk<sup>4</sup>.

The total sulphur found in four fractional precipitations of this substance was the following :

TABLE XXII.—PERCENTAGE OF TOTAL SULPHUR IN OVOVITELLIN.

2	3	4	5
1.046	1.000	1.047	1.026

The average of these figures gives 1.028 per cent. of total sulphur. The amount of loosely bound sulphur was found to be the following :

<sup>1</sup> *Pflüger's Archiv.*, 43, 244.

<sup>2</sup> *Rendic della R. Accad. delle Scienze di Napoli*, fasc. 3-5, 1894.

<sup>3</sup> *Loc. cit.*

<sup>4</sup> Osborne and Campbell: Report Connecticut Agricultural Experiment Station for 1899; also *This Journal*, 22, 413.

TABLE XXIII.—PERCENTAGE OF LOOSELY BOUND SULPHUR IN OVO-VITELLIN.

One gram with 30 per cent. NaOH and $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$ at $135^\circ$ . 2 hours.	Five grams with 30 per cent. NaOH and $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$ at $165^\circ$ . $5\frac{1}{4}$ hours.
0.367	0.357
0.320	....

The average of the higher of these figures, 0.362, probably closely represents the amount of sulphur split from ovovitellin by alkali.

*Casein from Cow's Milk.*

Chittenden and Painter<sup>1</sup> have made an extensive study of the composition of casein prepared in different ways and have confirmed Hammarsten's many analyses of this substance. Hammarsten<sup>2</sup> found by extensive and painstaking experiments that the total sulphur of casein was 0.78 per cent., Chittenden and Painter that it was 0.82 per cent. The average of these figures, 0.80 per cent., may therefore be taken for the total sulphur of casein.

The loosely bound sulphur was determined in a preparation of casein made from milk from which the fat had been thoroughly separated by centrifugation immediately after it had been drawn from the cow. Just enough hydrochloric acid was immediately added to precipitate the casein and this latter washed repeatedly by decantation, care being taken to keep it in a finely divided condition. The washed precipitate was dissolved by gradually adding portions of decinormal potassium hydroxide solution until all the casein redissolved. A milky appearing solution was so obtained which was perfectly neutral to very delicate violet litmus paper. This was filtered on a bed of filter-paper pulp and a perfectly clear filtrate obtained, which showed only a minute trace of opalescence. From this solution the casein was precipitated by hydrochloric acid, washed thoroughly by decantation with water, then with alcohol and finally dehydrated with absolute alcohol, and washed with ether. Less than nine hours elapsed from the time the milk was taken from the cow until the preparation was put under alcohol.

TABLE XXIV.—PERCENTAGE OF LOOSELY BOUND SULPHUR IN CASEIN.

Five grams with 30 per cent. NaOH and $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$ at $165^\circ$ . 3 hours.
0.103
0.099

<sup>1</sup> Chittenden and Painter: Studies from the physiol. lab. of Yale University, II, p. 156.

<sup>2</sup> Hammarsten: *Zschr. physiol. Chem.*, 7, 269.

The average of these figures, 0.101, shows that a very much smaller proportion of the total sulphur can be obtained from casein as sulphide than from any of the other proteins. The amount obtained agrees closely with that found by Fleitmann;<sup>1</sup> namely, 0.07 per cent.

#### IV. RELATION OF TOTAL SULPHUR TO THE PROTEIN MOLECULE.

An examination of the figures obtained in determining total sulphur shows that all the proteins examined, with the exception of vicilin, phaseolin, and conglutin, contain a constant proportion of sulphur. Those proteins which can be obtained in crystals, and therefore be made quite pure, show such a uniform proportion of sulphur that there can be no doubt whatever that this is a definite constituent of their molecules. If now, as was proposed at the beginning of this paper, we calculate the simplest empirical formulas for these proteins and also for some of the other more carefully prepared and analyzed animal proteins, and multiply the figures obtained by such a whole number as shall give a molecular weight nearest to 15,000, we shall obtain the formulas given in Table XXV. Such formulas are, of course, to be regarded as only approximate, since the methods of analysis preclude great accuracy. Carbon and nitrogen can be determined with sufficient precision to give figures falling within a few atoms of the truth, but a slight error in determining sulphur leads to serious differences in the formulas. An error of 10 per cent. of the total sulphur leads to an error of about 65 atoms of carbon and 20 atoms of nitrogen. If the protein contains but 0.4 per cent. of sulphur, such an analytical error would equal 0.04 per cent. An examination of the figures obtained in determining total sulphur indicates that the average amount found for each protein is probably within 0.04 per cent. of the amount actually present. For proteins containing more than 0.4 per cent. of sulphur, the probable error in the formulas is correspondingly decreased, so that for those containing 0.8 per cent. of sulphur it need not much exceed 30 atoms of carbon and 10 atoms of nitrogen, and for a protein which, like ovalbumin, contains 1.6 per cent. of sulphur, the error does not amount to more than about 15 atoms of carbon and 5 atoms of nitrogen. Whether or not the proteins in fact have similar molecular weights, must remain for future investigation to show, but in the meantime the formulas given in the table seem worthy of consideration since they suggest relations not otherwise apparent.

<sup>1</sup> Fleitmann: *Loc. cit.*

TABLE XXV.—COMPOSITION AND POSSIBLE EMPIRICAL FORMULAS OF SOME PROTEIN BODIES.

	Composition.					Formula.					Molecu- lar weight.				
	Car- bon.	Hydro- gen.	Nitro- gen.	Sul- phur.	Iron.	Phos- phorus.	Oxy- gen.	Car- bon.	Hydro- gen.	Nitro- gen.		Sul- phur.	Iron.	Phos- phorus.	Oxy- gen.
Vegetable Proteins.															
Amazulin .....	51.30	6.90	19.32	0.429	....	....	22.081	638	1030	206	2	..	..	206	14930
Vignin .....	52.64	6.95	17.25	0.426	....	....	22.734	660	1040	185	2	..	..	214	15038
Legumin .....	51.72	6.95	18.04	0.385	....	....	22.995	718	1158	214	2	..	..	238	16642
Zein .....	55.23	7.26	16.13	0.600	....	....	20.78	736	1161	184	3	..	..	208	15993
Glycinin .....	52.12	6.93	17.53	0.710	....	....	22.71	780	1248	206	4	..	..	255	17700
Hordein .....	54.29	6.80	17.21	0.847	....	....	20.53	675	1014	181	4	..	..	194	14880
Edestin .....	51.50	7.02	18.69	0.88	....	....	21.91	624	1021	193	4	..	..	199	14523
Bynin .....	55.03	6.67	16.26	0.84	....	....	21.20	706	1026	180	4	..	..	204	15410
Glialin .....	52.72	6.86	17.66	1.027	....	....	21.733	685	1068	196	5	..	..	211	15568
Excelsin .....	52.18	6.92	18.30	1.086	....	....	21.514	642	1018	192	5	..	..	198	14738
Leucosin .....	53.02	6.84	16.80	1.280	....	....	22.06	663	1026	180	6	..	..	207	15006
Animal proteins.															
Globin .....	54.98	7.20	16.89	0.42	....	....	20.51	700	1098	184	2	..	..	196	15274
Fibrin .....	52.68	6.83	16.91	1.10	....	....	22.48	645	1004	178	5	..	..	207	14708
Seroglobulin, horse .....	52.71	7.01	15.85	1.11	....	....	23.32	628	1002	160	5	..	..	209	14310
Fibrinogen .....	52.93	6.90	16.66	1.25	....	....	22.26	679	1062	183	6	..	..	207	15276
Myosin .....	52.82	7.11	16.67	1.27	....	....	22.03	660	1074	181	6	..	..	208	15048
Ovalbumin .....	52.75	7.10	15.51	1.616	....	....	23.024	696	1125	175	8	..	..	220	15703
Lactalbumin .....	52.19	7.18	15.77	1.73	....	....	23.13	644	1064	166	8	..	..	214	14792
Seralbumin, horse .....	52.99	7.01	15.93	1.93	....	....	22.14	662	1051	171	9	..	..	207	14989
Seralbumin, human exudation .....	52.25	6.65	15.88	2.25	....	....	22.95	684	1045	178	11	..	..	225	15697
Composed proteins.															
Oxyhemoglobin, horse .....	54.64	7.09	17.38	0.39	0.335	....	20.165	758	1181	207	2	1	..	210	16655
Oxyhemoglobin, dog .....	54.57	7.11	16.38	0.368	0.336	....	21.036	758	1185	195	3	1	..	219	16667
Casidin .....	53.13	7.06	15.78	0.80	0.86	0.86	22.37	708	1130	180	4	..	..	224	15982
Ovovitelin .....	51.56	7.12	16.23	1.028	....	0.82	23.242	671	1112	182	5	..	..	227	15628



The analyses of the vegetable proteins given in the preceding table were made by the writer and his associates in this laboratory; those of globin and serum albumin are by Schulz;<sup>1</sup> those of fibrin,<sup>2</sup> fibrinogen,<sup>3</sup> serum globulin,<sup>3</sup> serum albumin,<sup>3</sup> from human exudation are by Hammarsten; that of casein is the average of a large number of closely agreeing analyses, of many preparations, made by Hammarsten<sup>4</sup> and by Chittenden and Painter;<sup>5</sup> that of myosin is the average of many closely agreeing analyses of different preparations obtained from several species of animals by Chittenden and Cummins;<sup>6</sup> and that of lactalbumin is by Sebelien.<sup>7</sup>

The figures given in the table for the oxyhemoglobins require explanation since it seems to be generally assumed that the composition of these bodies is still uncertain. The following analyses of oxyhemoglobin from the horse have been published:

Carbon.	Hydrogen.	Nitrogen.	Sulphur.	Iron.	
54.87	6.97	17.31	0.65	0.47	Hoppe-Seyler and Kossel. <sup>8</sup>
54.74	7.03	17.28	0.67	0.45	Otto. <sup>9</sup>
54.40	7.20	17.61	0.65	0.47	Büchler. <sup>10</sup>
51.15	6.76	17.94	0.39	0.335	Zinoffsky. <sup>11</sup>
....	....	....	0.44	0.39	Hoppe-Seyler. <sup>12</sup>
54.56	7.15	17.33	0.43	....	Schulz. <sup>13</sup>
....	....	....	....	0.469	Lawrow. <sup>14</sup>

In conjunction with Bunge, Zinoffsky determined iron, both gravimetrically and volumetrically, with the utmost care, using very large quantities of oxyhemoglobin, from 10 to 60 grams, and making many determinations in three different preparations. None of the other analysts offer any evidence that their figures were obtained under conditions which entitle them to acceptance rather than those given by Zinoffsky. The fact that the ratio

<sup>1</sup> Schulz: *Loc. cit.*

<sup>2</sup> Hammarsten: *Pflüger's Archiv.*, 22, 489.

<sup>3</sup> Hammarsten: *Jahresbericht. f. Thierchem.*, 11, 19.

<sup>4</sup> Hammarsten: *Ztschr. physiol. Chem.*, 7, 269.

<sup>5</sup> Chittenden and Painter: "Studies from the Laboratory of Physiological Chemistry," Vol. II., p. 156.

<sup>6</sup> Chittenden and Cummins: *Ibid.*, Vol. III, p. 156.

<sup>7</sup> Sebelien: *Ztschr. physiol. Chem.*, 9, 463.

<sup>8</sup> Hoppe-Seyler: *Ibid.*, 2, 149.

<sup>9</sup> Otto, quoted by Hüfner: *Ibid.*, 8, 358.

<sup>10</sup> Büchler, quoted by Hüfner: *Ibid.*, 7, 59.

<sup>11</sup> Zinoffsky: *Ibid.*, 10, 16.

<sup>12</sup> Hoppe-Seyler: "Handbuch, physiol. and pathol. chem. Analyse," 1893.

<sup>13</sup> Schulz: *Ztschr. physiol. Chem.*, 24, 469.

<sup>14</sup> Lawrow: *Ibid.*, 26, 343.

between the iron and sulphur, as given by Zinoffsky, is strictly as 1 : 2, is evidence of the accuracy of his determinations, since there is every reason to believe that oxyhemoglobin is a definite compound containing hematin and protein in a molecular proportion. On the other hand, the fact that a definite ratio does not exist between the figures given by the other investigators indicates either a lack of purity in the preparations analyzed or inaccuracy of analysis.

The amount of sulphur given in these analyses differs widely. There is no evidence, however, that any of these analysts, except Zinoffsky, used unusual care in determining sulphur. Zinoffsky subjected his methods for determining sulphur to a very rigid test and employed about 10 grams of oxyhemoglobin, for each of six determinations. The results obtained with three different preparations fell between 0.3916 and 0.3583. It is to be noted that the later determinations of sulphur by Hoppe-Seyler and Schulz agree with those of Zinoffsky much more closely than they do with the other earlier determinations.

All these analyses agree fairly well for carbon, hydrogen and nitrogen except that given by Zinoffsky, which differs much from the other analyses. Hüfner has suggested that this was caused by the method employed by Zinoffsky in preparing his oxyhemoglobin, but this cannot be true, because, as Jaquet points out, Zinoffsky made the preparation that he analyzed by the same method the other investigators employed. It seems more probable that the differences between Zinoffsky's figures for these elements and those of the others are analytical.

For the composition of oxyhemoglobin from the horse, I have given in the table Zinoffsky's figures for iron and sulphur, together with the average of the figures given by the other analysts for carbon, hydrogen, and nitrogen.

In conjunction with Bunge, Jaquet<sup>1</sup> analyzed oxyhemoglobin from dog's blood and determined sulphur and iron with the same precautions and the same care that Zinoffsky used in determining these elements in oxyhemoglobin from horse blood.

But one other analysis of this substance appears to be on record, made by Hoppe-Seyler,<sup>2</sup> which does not differ very widely from Jaquet's except for sulphur.

As I have been able to confirm the accuracy of Jaquet's

<sup>1</sup> *Ztschr. physiol. Chem.*, 14, 289.

<sup>2</sup> "Med. chem. Untersuch," p. 370.

figures for sulphur, I have given in the table the average of them, omitting one determination of hydrogen which is manifestly too high.

# V. RATIO OF LOOSELY BOUND TO TOTAL SULPHUR.

In most of the proteins examined in this investigation, as well as in those examined by others, the loosely bound sulphur is approximately a simple fraction, as the following table shows :

TABLE XXVI.—RATIO OF LOOSELY BOUND TO TOTAL SULPHUR.

Protein.	Total sulphur.	Loosely bound sulphur.	Per cent. of total sulphur as loosely bound.
Seralbumin.....	1.930 <sup>1</sup>	1.280 <sup>1</sup>	66
Oxyhemoglobin, dog .....	0.568 <sup>2</sup>	0.335	59
Serglobulin, horse.....	1.110 <sup>3</sup>	0.630 <sup>1</sup>	57
Gliadin .....	1.027	0.619	60
Oxyhemoglobin, horse.....	0.380 <sup>4</sup>	0.190 <sup>1</sup>	50
Vignin.....	0.426	0.214	50
Amandin.....	0.429	0.217	50
Globin .....	0.420 <sup>1</sup>	0.200 <sup>1</sup>	48
Glycinin .....	0.710	0.320	46
Vicilin .....	0.200	0.092	46
Legumin .....	0.385	0.165	41
Edestin .....	0.880	0.346	40
Zein .....	0.600	0.212	35
Ovovitellin .....	1.028	0.348	34
Fibrin .....	1.100 <sup>5</sup>	0.380 <sup>6</sup>	34
Excelsin .....	1.086	0.350	32
Ovalbumin .....	1.616	0.491	30
Phaseolin .....	0.312	0.072	23 <sup>1</sup> / <sub>4</sub>
Casein .....	0.800 <sup>7</sup>	0.101	13 <sup>1</sup> / <sub>6</sub>

Leaving phaseolin and casein out of consideration for the present, it might be assumed that the protein molecule contains either 2 or 3 atoms of sulphur. Such an assumption presupposes, however, that in most cases the whole of the loosely bound sulphur can be converted into lead sulphide under the conditions of our experiments. The results obtained with edestin indicate plainly that one-half of its sulphur can not be thus separated since the highest figures found fell short of one-half of the total

<sup>1</sup> Schulz: *Loc. cit.*

<sup>2</sup> Jaquet: *Loc. cit.*

<sup>3</sup> Hammarsten: *Pflüger's Archiv.*, 22, 489.

<sup>4</sup> Zinoffsky: *Loc. cit.*

<sup>5</sup> Hammarsten: *Pflüger's Archiv.*, 22, 479.

<sup>6</sup> Krüger: *Loc. cit.*

<sup>7</sup> Hammarsten: *Loc. cit.*, and Chittenden and Painter: *Loc. cit.*

sulphur by a quantity decidedly in excess of any probable analytical error. On the other hand, nearly all fell distinctly above one-third. If this is true for edestin it may also be true for some of the other proteins; thus in excelsin the loosely bound sulphur falls short of two-fifths of the total by nearly the same proportion that it falls short of one-half in edestin. We should, therefore, consider whether or not the proportion of loosely bound sulphur agrees with a definite number of the sulphur atoms given in Table XXV quite as well as with these simple fractions.

In the following table these proteins are given, arranged in the order of their sulphur content; the number of atoms of fixed and loosely bound sulphur with which the results of the determinations agree most closely, assuming the number of atoms of sulphur contained in the molecule to be that shown in Table XXV, the percentage of loosely bound sulphur found in these proteins; the percentage calculated for the number of atoms of sulphur assumed to be split off; the difference between the amount found and that calculated; and the percentage of the calculated quantity that the amount found is equal to.

TABLE XXVII.—ATOMS OF FIRMLY AND LOOSELY BOUND SULPHUR.

Protein.	Total sulphur.	Atoms of fixed sulphur.	Atoms of loosely bound sulphur.	Percentage of loosely bound sulphur found.	Percentage of loosely bound sulphur calculated.	Differences between found and calculated.	Percentage of the calculated formed by that found.
Legumin .....	0.385	1	1	0.165	0.193	—0.028	81
Oxyhemoglobin, horse...	0.390	1	1	0.190	0.195	—0.005	97
Globin, horse .....	0.420	1	1	0.200	0.210	—0.010	95
Vignin .....	0.426	1	1	0.214	0.213	+0.001	100
Amandin .....	0.429	1	1	0.217	0.213	+0.004	104
Oxyhemoglobin, dog....	0.568	1	2	0.335	0.379	—0.037	88
Zein.....	0.600	2	1	0.212	0.200	+0.012	106
Glycinin.....	0.710	2	2	0.320	0.355	—0.035	90
Hordein .....	0.847	2	2	0.348	0.423	—0.075	83
Edestin.....	0.880	2	2	0.347	0.440	—0.093	79
Gliadin.....	1.027	2	3	0.619	0.629	—0.010	99
Ovovitellin .....	1.028	3	2	0.348	0.410	—0.062	83
Excelsin.....	1.086	3	2	0.350	0.430	—0.080	81
Serglobulin, horse.....	1.110	2	3	0.630	0.666	—0.036	95
Fibrin .....	1.100	3	2	0.380	0.440	—0.060	86
Ovalbumin .....	1.616	5	3	0.491	0.609	—0.118	81
Seralbumin, horse .....	1.930	2	7	1.280	1.498	—0.218	85

The amount of loosely bound sulphur found in those proteins which appear in this table as containing but one atom of such sulphur agrees almost exactly with that calculated. Of those in which a larger number of atoms appear as loosely bound, the majority show a deficiency in the amount found compared with that calculated.

Before a decision can be reached as to the proportion of loosely bound sulphur actually contained in the molecules of these different protein bodies, it is necessary to know whether all such sulphur can be obtained as lead sulphide under the conditions of the experiments described in this paper. All investigators who have undertaken to determine the proportion of loosely bound sulphur in the proteins have noted the similarity of the behavior of these substances to that of cystin under similar conditions. Cystin, however, had never been detected among the decomposition products of protein bodies until K. A. H. Moerner<sup>1</sup> recently found it in quantity among those of horn, 6.8 per cent.; of egg membrane, 6 per cent.; of human hair, 12.6 per cent.; and of serum albumin, over 1 per cent.

He also found in the solutions from which the cystin had been separated a not inconsiderable quantity of sulphur which, on treatment with sodium hydroxide and lead acetate, yielded lead sulphide. To what complex this latter sulphur belonged, Moerner did not determine.

Embden<sup>2</sup> has very recently confirmed Moerner's observations by investigations undertaken independently and without a knowledge of the latter's results. Embden isolated cystin in quantity from horn and found among the products obtained from serum and egg albumin and edestin, cystein, which latter substance he considers to be the primary decomposition product of these protein bodies, the cystin being a secondary product.

From these recent observations of Moerner's and Embden's, it is highly probable that a part of the loosely bound sulphur of many protein bodies belongs either to a cystein or a cystin complex. If this is so, the results obtained in attempting to determine quantitatively the proportion of loosely bound sulphur in such proteins as contain this group must necessarily fall short of the total quantity of sulphur belonging to the cystein or cystin

<sup>1</sup> Moerner: *Ztschr. physiol. Chem.*, 28, 595 (1899) and Proc. 13th Inter. Cong. Med. Sec. d. Physiol., etc., p. 15, Paris, 1900.

<sup>2</sup> Embden: *Ztschr. physiol. Chem.*, 32, 94 (1901).

radical, for it is well known that a part only of the sulphur of these two substances can be converted into lead sulphide by boiling with solutions of sodium hydroxide and lead acetate.

Thus Baumann and Goldmann,<sup>1</sup> by heating cystin with 10 per cent. sodium hydroxide and lead acetate for nine hours, got only 68 per cent of the sulphur. Suter,<sup>2</sup> by heating for thirty-three and one-half hours, obtained 83 per cent., and Schulz,<sup>3</sup> by boiling cystin with 30 per cent. sodium hydroxide, zinc, and bismuth oxide for ten hours, obtained as sulphide 53 per cent.; by boiling for twenty-five hours, 53.7 per cent.; by heating in an atmosphere of hydrogen for ten hours at 105°-110°, 52.4 per cent., and by boiling cystein for ten hours, 52 per cent. of the total sulphur contained in the substance.

In view of these facts it would seem probable that from most proteins, especially those rich in sulphur, we cannot obtain all of the loosely bound sulphur.

An examination of the figures of Table XXV shows that, with but three exceptions, the loosely bound sulphur obtained from those proteins which contain more than 0.43 per cent. of sulphur formed from 79 to 90 per cent. of the calculated, while the amount obtained from those containing less than 0.43 agreed with that calculated well within the limits of accuracy of analysis.

The amount of loosely bound sulphur found in all those proteins which appear in the table to contain but one atom of such sulphur agrees in every case with the calculated quantity more closely even than could be expected, while with but one exception, in all those proteins which appear as containing more than one atom of loosely bound sulphur, the quantity found is distinctly less than that calculated.

These facts may find an explanation in Moerner's observations of two sulphur-containing complexes, both of which yield lead sulphide on treating with alkaline lead solutions. It may well be that cystein or cystin is a constituent of only those proteins which are comparatively rich in sulphur, so that from these but a part of the sulphur belonging to these complexes can be obtained as sulphide, while from the others containing only the other complex observed by Moerner, all of the sulphur can be obtained. The amount of loosely bound sulphur actually found in edestin

<sup>1</sup> Baumann and Goldmann : *Ztschr. physiol. Chem.*, 12, 257 (1888).

<sup>2</sup> Suter : *Ibid.*, 20, 564 (1895).

<sup>3</sup> Schulz : *Loc. cit.*

agrees well with such a supposition, for if 1 atom of sulphur belongs to a complex yielding all its sulphur as sulphide we would obtain 0.22 per cent. from this source, and if another atom belongs to cystein (Embden has obtained cystein from edestin), which according to Schulz yields about one-half its sulphur as sulphide, from this we would obtain about 0.11 per cent., making 0.33 per cent. in all, which agrees closely with the 0.347 per cent. found. The deficiency found for most of the proteins here represented as containing more than 1 atom of loosely bound sulphur is nearly equal to that which would occur if these contained 1 molecule of cystein, except for serum albumin, in which the deficiency corresponds to 2 molecules of cystein or 1 of cystin.

In conclusion, attention should be called to casein, which presents a marked contrast to all the other proteins examined, in the fact that only one-eighth of the total sulphur was obtained as sulphide. If the complex which contains this sulphur yields all its sulphur as sulphide, the molecular weight of casein cannot be less than 30,000; if, on the other hand, it yields only a part of its sulphur as sulphide, it presents a marked contrast to the other protein substances which contain but little loosely bound sulphur, for these yield almost exactly one-half of their total sulphur as sulphide, which strongly indicates that all the sulphur of the complex containing this is converted into lead sulphide. Of all the proteins examined, casein yields by far the smallest proportion of loosely bound sulphur.

RESEARCH LABORATORY OF THE CONNECTICUT  
AGRICULTURAL EXPERIMENT STATION.

---

## THE PEROXIDE CALORIMETER AS APPLIED TO EUROPEAN COALS AND PETROLEUM.

BY S. W. FARR.

Received September 3, 1901.

AT the suggestion of Dr. Lunge, the calorimeter recently described in this Journal<sup>1</sup> has been subjected to a series of tests on European coals. The Zurich laboratory afforded especially good facilities for the work and I am indebted to Dr. Lunge for putting them at my disposal. Much credit is also due his assistant, Mr. Offerhaus, whose very efficient help made it possi-

<sup>1</sup> This Journal, 22, 646.

ble to accomplish the large number of tests in the limited time available.

It was evident at the outset that the combustion of European coals offered a somewhat new and different proposition from that of the soft coals of the United States. Their anthracitic character and smaller percentage of bituminous matter made their combustion more difficult and in many cases incomplete. Experience had already shown that certain substances, as, for example, coke or sugar carbon, gave incomplete combustions when used alone with sodium peroxide. The two devices before suggested for overcoming the difficulty were fine pulverization and the addition of an accelerator in the shape of a weighed quantity of some good soft coal whose combustion factor had been carefully determined. Such soft coals in Europe, however, are the exception and the above expedient seemed impracticable as well as not altogether satisfactory in the very hard anthracites met with.

It was, therefore, necessary to increase the oxidizing power of the peroxide. From data already at hand it was evident that this could be accomplished in a measure by use of some free burning organic material as a good soft coal, sugar, etc. The effect of superoxides had also been tried, as barium peroxide, potassium chlorate, etc. Continuing along this line, the details of which are here omitted, it was found that a very intense oxidizing effect was secured by the use of a mixture of potassium persulphate and tartaric acid, 1 gram of the former to 0.5 gram of the latter, carefully weighed out; this with about 12 grams of sodium peroxide and 0.5 gram of the coal to be tested gave very complete combustions. A soft iron wire, of No. 10 or 2.5 mm. gauge and 1 cm. long, was used for igniting. Other wire as of copper, nickel, silver, etc., will melt and burn to a greater or less extent, hence cannot be used. The factors already determined were found to apply also to these coals; *viz.*, 73 per cent. of the total heat due to combustion and 27 per cent. due to the heat of combination of the products.

The results obtained in the table below are on samples kindly furnished by Professor Dr. Constam, Zürich, who had determined the Mahler factors and to whom we were further indebted for the use of his very exact thermometer carefully calibrated by himself.



TABLE I.

	Coals.	Water.	Ash.	Calories by Mahler apparatus.	Calories by sodium peroxide.	Variations from Mahler.	Chemicals used in addition to 12.5 to 13.5 grams of sodium peroxide.
No. 277,							
Ruhr flame coal.....	2.6	7.1	7685	7695	+10	0.6 tartaric acid.	
No. 278,							
Ruhr coal.....	1.3	6.6	8059	8075	+16	{ 0.5 tartaric acid. 1.0 pot. persulph.	
No. 282,							
Anthracite coal... ..	1.5	6.7	7981	7990	+ 9	0.6 tartaric acid.	
No. 285,							
Coke .....	0.6	13.0	6640	6687	+47	0.5 tartaric acid.	
No. 289,							
Anthracite, Wales...	2.0	4.2	8049	8021	-28	0.6 tartaric acid.	
No. 308,							
English anthracite..	2.4	4.6	8365	8326	-39	{ 0.5 tartaric acid. 1.0 pot. persulph.	
No. 312,							
Belgian "Braisettes".	2.4	10.7	7409	7394	-15	0.5 tartaric acid.	
No. 324,							
Saar coal.....	4.9	11.7	6594	6634	+40	0.5 tartaric acid.	
No. 326,							
Cardiff coal.....	2.2	7.2	7872	7936	+64	0.5 tartaric acid.	
No. 331,							
Saar coal.....	3.5	8.4	7146	7184	+38	0.5 tartaric acid.	
Brown coal.....	15.17	..	5037	5076	+39	1.0 of coal used, no extra chemical.	

When the water content exceeds 2.5 or 3 per cent. it should be removed and the combustion made on the oven-dried sample. For example, the last number in the table, that of brown coal, has over 15 per cent. of water. A combustion with sodium peroxide in case of this sample without the water removed gives approximately 300 calories excess, or 20 calories for each per cent. However, not enough data is at hand to fully establish a correction for the water content.

Tartaric acid combining with sodium peroxide may be determined by mixing in the cartridge 0.5 gram of the finely ground acid with about 6 grams of peroxide, and igniting with a wire in the usual manner. The result of a number of such determinations indicated, for the material used in these tests, a factor for the tartaric acid, including the wire  $0.85^{\circ}$  per 0.5 gram and for the potassium persulphate  $0.155^{\circ}$  per 1 gram. Soft iron wire 2.5

mm. by 1 cm. long and weighing approximately 0.4 gram at an estimated temperature of  $700^{\circ}$ , carries into the mass 0.015° of heat. Hence, in using the combined chemicals above with but one wire the total correction factor is  $0.99^{\circ}$ . However, with any given set of reagents a blank determination should be made. Variations may arise from the potassium persulphate and tartaric acid employed and also from the moisture absorbed by the sodium peroxide. In the latter case, the effect of any hydrated sodium peroxide,  $\text{Na}_2\text{O}_2 + 2\text{H}_2\text{O}$ , may be measured or neutralized as may be desired by enclosing the usual amount alone in the cartridge and submerging in boiling water for five to ten minutes, cooling, opening, and adding the charge, then proceeding as usual.

With the above combination of persulphate and tartaric acid a complete oxidation of substances may be secured which, before, behaved indifferently with peroxide alone.

In illustration of this point a sample of crude oil from Beaumont, Texas, gave the results as follows, the Mahler determinations being made by Mr. Koch, of the University of Illinois:

CRUDE OIL.		Calories.
Mahler factor.....		10644
New method (a).....		10654
“ “ (b).....		10600
“ “ (c).....		10637
“ “ (d).....		10665
Average, last four.....		10639

The method while varying in no essential from that used for coals should, perhaps, be outlined, thus:

After preparing the cartridge and screwing the bottom on firmly, there is added about  $1/4$  measure (3 grams) of sodium peroxide. Upon this is dropped about  $1/3$  of a gram (30 drops) of petroleum, using a dropping pipette from a light weighing-flask, the exact weight of oil taken being determined by difference. There is now added the 1 gram of finely powdered potassium persulphate and 0.5 gram of powdered tartaric acid. This mixture is stirred with a wire to break up any lumps and make an even mixture. Now add one measure of sodium peroxide, clean the wire in this upper layer, jar off the adhering particles and remove the wire, screw on the top with valve, and shake thoroughly. Place in the calorimeter and ignite, using a soft iron wire.

The calculation is made by first subtracting the factor obtained by running the mixture of chemicals as above described, omitting the oil. The remainder  $r$  gives the rise in temperature due to the combustible; 73 per cent. of this is due to the heat of combustion, and 27 per cent. to the heat of combination of the chemical products, hence,

$$\frac{r \times 0.73 \times \text{wt. of water}}{\text{wt. of oil}} = \text{calories per kilo.}$$

A homogeneous mixture may result from simply shaking, and without the use of the wire. Indeed, some of the above results were so obtained, but in general it is better to mix by stirring as described.

It is a convenience to have a thoroughly triturated mixture of potassium persulphate and tartaric acid carefully adjusted to the proportions above indicated. It is then necessary to make but one weighing and, of course, 1.5 grams of the mixture are taken.

ZURICH, July, 1901.

## STUDIES IN NITRIFICATION.\*

BY J. G. LIPMAN.

Received October 18, 1901.

IN undertaking the work submitted here it was intended to study nitrification in its bearing to practical agriculture. The aim was to investigate in how far certain conditions influence the production of nitrates in the soil, in how far the application of the various fertilizers promote or retard nitrification, and in how far the moisture conditions modify this. Much work has already been done on the subject, notably by the French investigators, and in the light of our present knowledge we have come to modify many of the older methods of husbandry, so as to bring them in agreement with recent facts. Yet great as is the service rendered to agriculture by the research of the last two decades, the conclusions reached are by no means final in every case; nor have all of the questions raised by the work been satisfactorily answered. Much of our knowledge on nitrification is rather obscure; many questions still await solution. We know now that plants take up most of their nitrogen in the form of nitrate; we know that the conversion of organic nitrogen into ammonia, nitrite, and nitrate is effected by living organisms; we know, to a great extent, what conditions are favorable or injurious to the development of these

\* Abstract from Master's Thesis, Cornell University, 1900.

organisms, but we do not know just *how* the micro-organisms oxidize ammonia nitrogen to nitrite or nitrate nitrogen; we are not yet certain as to the exact relations in the soil of the nitrifying, denitrifying, and, what Beijerinck<sup>1</sup> calls the "oligo nitrophile" organisms to one another; we have much to learn as to the physiology and morphology of these organisms. Standing alone, neither chemistry nor bacteriology can solve the problem fully. If it is to be solved at all, as we hope it will, it will be by the combined efforts of chemistry and bacteriology.

It is not claimed that the work reported in the following pages is, all of it, strictly original. The same ground has, partly at least, been covered by others; nevertheless, even in such cases the conditions and methods were not the same, and it is hoped that the results obtained will be of value to the student of agriculture. It should be stated here that this work was intended to be little more than preliminary. It was more than anything else a study of methods and conditions, only a preparation for a more critical and more extended study of the same phenomena, which it is hoped may be continued in the future.

Now as to the methods: For the determination of organic and of total nitrogen, the Kjeldahl and the Kjeldahl modified<sup>2</sup> methods were used. The Ulsch<sup>3</sup> and the phenolsulphonic acid<sup>4</sup> methods were used for the determination of nitrates. Of the different methods proposed for the determination of nitrites in the presence of nitrates the method first proposed by Griess<sup>5</sup> and known as the sulphanilic acid and naphthylamine method was selected because of its convenience and delicacy. Ammonia was determined by distillation with soda or magnesia, and titration against standard acid or by nesslerizing. For qualitative tests there were also used metaphenylenediamine for nitrites, and brucine and diphenylamine for nitrates.

For the study of nitrification three soils were used.

1. A calcareous sand containing

0.017 per cent. of total nitrogen,  
0.00083 per cent. of nitrate nitrogen,  
0.00003 per cent. of nitrite nitrogen.

<sup>1</sup> *Centr. für. Bact.*, 1901, p. 561.

<sup>2</sup> Wiley's "Agricultural Analysis," Vol. II, 215.

<sup>3</sup> *Chem. Centr.*, 2, 926 (1890).

<sup>4</sup> Mason's "Examination of Water," p. 44.

<sup>5</sup> *Ztschr. anal. Chem.*, 18, 597; *Ztschr. angew. Chem.*, (1889), p. 666; *Bull. Soc. Chim.* [3], 2, 347.

2. A loam soil from the college farm, Ithaca, N. Y., containing  
0.201 per cent. of total nitrogen,  
0.004 per cent. of nitrate nitrogen,  
0.00002 per cent. of nitrite nitrogen.
3. An artificial greenhouse soil rich in organic matter and coal ashes, and containing  
0.0139 per cent. of nitrate nitrogen,  
0.00008 per cent. of nitrite nitrogen.

The complete extraction of the nitrites and nitrates formed in the soil was one of the first problems encountered. A number of devices for accomplishing the purpose were tried with varying success. The final mode of procedure was as follows: 100 grams of soil were shaken in a 2-liter bottle, provided with a stopper, with 1 liter of distilled water. After shaking for five minutes the liquid holding the nitrites and nitrates in solution was filtered, about a gram of freshly precipitated and washed aluminum cream added to the filtrate and the latter shaken. It was then filtered again, 100 cc., representing one-tenth of the nitrates held in solution, carefully measured off for the determination of nitrates, and 100 cc. for the determination of nitrites.

#### THE SULPHANILIC ACID AND NAPHTHYLAMINE METHOD.

This is a very delicate method, being capable of distinguishing 1 part of nitrogen as nitrous acid in 1,000,000,000 parts of water. It is easy of manipulation and peculiarly well adapted for the determination of nitrites in soil leachings. The details of manipulation are: 100 cc. of the filtered and charified soil leachings are placed in a colorimeter, 1 cc. each of sulphanilic acid and naphthylamine solutions added, the contents well shaken and allowed to stand for thirty minutes. 100 cc. of distilled water are similarly treated in another colorimeter to which a known amount of standard sodium nitrite is also added. At the end of thirty minutes the depths of color are compared, and the nitrite content in the sample determined.

#### THE PHENOLSULPHONIC ACID METHOD.

The details of this method as observed in the work reported below are as follows: 100 cc. of the filtered and clarified soil leachings are placed in a 125-150 cc. porcelain evaporating dish, 0.3 cc. of a saturated sodium carbonate solution added, and evap-

orated to dryness on a water-bath. Two cc. of phenolsulphonic acid are then added to the dry residue, and the latter is thoroughly moistened with it. About 15 cc. of distilled water are then introduced into the dish, and then enough ammonia to render the whole distinctly ammoniacal. The contents of the dish are next washed into a 100 cc. colorimeter, filled up to the mark with distilled water, and the depth of color compared with a standard in another colorimeter. It is important that the standard should be treated in precisely the same way as the unknown, and where chlorine is present in considerable quantities it should be determined and an equivalent quantity added to the standard. The addition of sodium carbonate is necessary where free nitric acid or ammonium nitrate are present, otherwise low results will be obtained. Where many determinations are made it is advisable for the sake of saving time to prepare a standard color solution. This is made as follows: 25 cc. of standard potassium nitrate solution (0.7221 gr. per liter) are treated as described above, the yellow liquid diluted to 1 liter and kept in stock. Every cubic centimeter of this solution corresponds to 0.0025 mg. of nitrogen as nitrate. On the whole the method has been followed as given in Mason's "Examination of Water."

The method as thus employed was eminently satisfactory, and leaves nothing to be desired when the quantities of nitrate present are small, and when care is taken to treat the standard and the unknown in exactly the same way. When, however, the amount of nitrate nitrogen exceeds 25 mg. per liter, great care is required in the readings if accurate results are to be obtained, although with experience close determinations can be made with 40 to 50 mg. of nitrate nitrogen per liter. For solutions containing greater quantities than 50 mg. of nitrate nitrogen per liter the Ulsch method was used. Many difficulties were encountered while working with this method, and about 100 determinations were made of known solutions before results were obtained that were entirely satisfactory. It was found necessary to observe the following precautions to insure accurate results:

1. Blank determinations should be made to allow for the nitrogen in the reagents, especially for that in the iron dust.
2. Five grams of iron should be used to not more than 0.5 gram of potassium nitrate.
3. Nine to ten cc. of sulphuric acid (1 : 1) give the best results.

4. The flask during reduction should be stopped up with a rubber stopper through which passes a funnel tube containing a few pieces of glass moistened with sulphuric acid.

5. The flask during reduction should be heated gradually to boiling, and the solution boiled until the evolution of hydrogen is over.

6. The contents of the flask should be diluted to about 250 cc.

7. Distillation should be carried on not too rapidly for at least forty-five minutes and until 150 cc. of the distillate has been collected. It is best to carry on the distillation nearly to dryness.

8. The greatest care should be taken that no rubber connections are exposed to the hot ammoniacal vapors.

In the first series of investigations the soil was sifted through a 7 mm. mesh sieve to remove pebbles and coarse particles, and about 3 pounds of that soil were placed in each of the 6-inch flower pots used. The latter were placed in porcelain saucers and water was added from below, it having been found from experience that this is the best way of preventing packing. Even with this method of watering it was necessary to stir the soil occasionally. While the experiment lasted the attempt was made to keep the soil at about 25 per cent. of its water content, that is, 3 pounds of air-dry soil to 1 pound of water. It was found, however, that under ordinary conditions it was very difficult to do it.

#### SERIES A.

No.	Sodium chloride. Gram.	Per acre.		Ammonium sulphate. Gram.
		Per cent.	Pounds.	
1	....	...	...	0.641
2	0.136	0.01	300	0.641
3	0.272	0.02	600	0.641
4	0.544	0.04	1200	0.641
5	1.360	0.1	3000	0.641
6	2.720	0.2	6000	0.641

This series was started on November 16th, and the moisture conditions were kept constant as far as was possible. The soil used was a clayey loam from the college farm. On January 10th, the six pots of the series were leached. The water ran through very slowly, and it took three days for about 1000 cc. of leachings to accumulate. At the end of that time the last portions of the leachings still gave a reaction for nitric acid with brucine, but none with diphenylamine. The color of the leachings indicated that where more salt was used more organic matter was

dissolved out of the soil ; and, moreover, where the larger quantities of salt were used the water ran through more rapidly. The leachings were then evaporated at 80° to dryness, the residue taken up with about 50 cc. of distilled water, filtered, washed and diluted to 100 cc. One-half of this was used for the determination of ammonia, the other half for the determination of nitrites and nitrates by the Ulsch method. After deducting the ammonia nitrogen and that of the blanks the following quantities of nitrite and nitrate nitrogen were obtained :

#### SERIES A.

No.	Mg.
1	20.89
2	16.06
3	18.60
4	18.86
5	24.47
6	24.21

In Series C, a coarse calcareous sand was used. Like the loam of Series A, it was sifted through a 7 mm. mesh sieve, and 3.5 pounds of that sifted sand were placed in each pot. In this series it was proposed to study the influence of stirring on nitrification.

#### SERIES C.

No.	Ammonium sulphate. Gram.	Stirred every day.			
13	....	"	"	"	"
14	0.641	"	"	"	"
15	0.641	"	"	three days.	"
16	0.641	"	"	"	"
17	0.641	"	"	seven	"
18	0.641	"	"	"	"

To insure nitrification a quantity of rich garden soil was shaken up with some water, and 5 cc. of the latter were added to each of the pots. The experiment lasted from November 21st until January 26th. At the end of that time the soils were leached, the water running through much more readily than it did in Series A. In a few hours leaching was complete, the last portion giving a very faint reaction with brucine. The leachings were evaporated in large dishes at 80° and treated as in Series A. The quantities of nitrite and nitrate nitrogen obtained by the Ulsch method were :



No.	Mg.
13	traces
14	traces
15	traces
16	traces
17	1.65
18	1.53

In Series D, the same quantities of calcareous sand were used as in Series C. Like the latter it was inoculated with 5 cc. of extract from a rich garden soil. The scheme of experiment was as follows :

SERIES D.		
No.	Ammonium sulphate. Gram.	Monopotassium phosphate. Grams.
19	1	0.017
20	1	0.170
21	1	1.700
22	1	0.017
23	1	0.170
24	1	1.700

The experiment began on November 25th, and ended on January 29th. As in Series A and C the Ulsch method was used, and the treatment in determining the nitrogen content of the different pots was exactly the same as in the preceding series. The following quantities of nitrite and nitrate nitrogen were obtained.

No.	Mg.
19	3.06
20	8.15
21	lost
22	5.86
23	2.55
24	4.34

In Series B the effect of sulphur on nitrification was studied. The subject has some practical significance, for quantities up to 400 or 500 pounds per acre have been used to prevent scab on potatoes. The soil used in this series of experiments was the same as in Series A, and, namely, a clay loam from the college farm, connected with Cornell University. The experiment began on November 21st and ended on January 13th. During that time the soils were kept moist, and at about 25 per cent. of water content. In this series the determinations of nitrite and nitrate nitrogen were made by the color methods: the former by the

Griess sulphanilic acid and naphthylamine method and the latter by the phenolsulphonic acid method. For the analytical data 100 grams of soil were taken from each pot after the entire mass had been carefully mixed, placed in a 2-liter bottle, 1 liter of distilled water added, and the contents shaken for five minutes. The water now holding the nitrates in solution was filtered, clarified with aluminum cream, and again filtered. The second filtrate now perfectly clear and colorless was placed in a stoppered flask after 100 cc. each were first drawn off for the determination of nitrates and nitrites respectively.

The scheme of experiment was as follows :

No.	Sulphur.		Per acre. Pounds.	Ammonium. sulphate. Gram.
	Per cent.	Gram.		
7	....	....	...	0.641
8	0.005	0.068	150	0.641
9	0.01	0.136	300	0.641
10	0.02	0.272	600	0.641
11	0.04	0.544	1200	0.641
12	0.1	1.360	3000	0.641

The quantities of nitrite and nitrate nitrogen found were :

No.	Nitrite. Mg.	Nitrate. Mg.
7	0.31	31.99
8	0.38	24.43
9	0.40	25.24
10	0.36	30.37
11	0.27	22.54
12	0.13	13.50

The results obtained in the above series were highly unsatisfactory. Instead of obtaining a gain in nitrate nitrogen there was a distinct loss. In Series A and B, where loam soil was used, there was present at the beginning of the experiment, as shown by the color method, 0.004 per cent. of nitrate nitrogen, and hence there was present in the 1350 grams of soil used 54 mg. of nitrogen as nitrate. At the end of the experiment the highest quantity of nitrate nitrogen found in any one sample in Series A was 24.47 mg. In other words, there was a loss of almost 30 mg. of nitrate nitrogen, and the results obtained, if they indicate anything at all, show that where sodium chloride was used at the rate of 3,000 and 6,000 pounds to the acre the loss of nitrate nitrogen was diminished. The deoxidation of the nitrates might

be ascribed here to denitrifying bacteria, and the fact that more nitrate was found where more sodium chloride was used would indicate that the latter prevented, to some extent, the denitrifying processes.

In Series B there was also a destruction of nitrates, but in this case the loss was the greatest where the greatest quantities of sulphur were used. Thus where sulphur was applied at the rate of 600 pounds to the acre the nitrate nitrogen found at the end of the experiment was 30.37 mg., while in the pots where the application was 1,200 and 3,000 pounds to the acre the nitrate nitrogen found at the end of the experiment was 22.54 mg. and 13.50 mg. respectively. In this case the nitrites and nitrates seemed to correspond to some extent, for in pots 11 and 12, where the least quantities of nitrate were found, there were also found the least quantities of nitrites. It is possible that the oxidation of large quantities of elementary sulphur in the soil may cause the destruction of nitrates without the intervention of micro-organisms. This point will bear further investigation.

In Series C and D, 1800 grams of air-dry soil were placed in each pot, and according to analysis by the color methods this air-dry sand contained 0.00083 per cent. of nitrate nitrogen, and 0.00003 per cent of nitrite nitrogen. In other words, there were present in each pot at the beginning of the experiment 14.94 mg. of nitrate nitrogen and 0.54 mg. of nitrite nitrogen. At the end of the experiments the nitrates and nitrites had practically disappeared in the soils of Series C, for in the samples stirred every day and every three days there were only traces of oxidized nitrogen present, while in the samples stirred once in seven days there was found about 1.5 mg. of oxidized nitrogen.

In Series D, containing the same amount of nitrates and nitrites as Series C, there was also a loss of oxidized nitrogen, except that the disappearance of the nitrates was not as complete as in the other case. The difference can hardly be attributed to either the ammonium sulphate or to the acid potassium phosphate, for there appears to be no correspondence in the quantities of nitrate nitrogen found, and the different amounts of the substances used.

Whatever the value of the results obtained in the above four series, they certainly were not a success as far as the production of nitrates is concerned. Whether the loss of nitrates was due to

insufficient aeration, or whether the constant variation in the moisture conditions was the cause of it, is hard to decide at present. It became apparent, however, that some other arrangement would be necessary in order that nitrification might be secured. Valuable data on the subject have been secured by a number of investigators who kept their soils in an atmosphere saturated with moisture. Acting accordingly, it was decided to study nitrification on 100 gram samples of soil placed in 750 cc. Erlenmeyer flasks.

#### FLASKS.

In Series J, 100 grams of calcareous sand were weighed off and placed in each of the flasks 1-10. The scheme of experiment was as follows:

Flasks.	Ammonium sulphate. Mg.	Water. cc.	Soil extract. cc.
1	100	8	1
2	100	8	1
3	100	9	1
4	100	9	1
5	100	10	1
6	100	10	1
7	100	11	1
8	100	11	1
9	100	12	1
10	100	12	1

The soil extract was obtained by shaking a quantity of rich greenhouse soil, in which nitrification was active, with some distilled water. As will appear from the above table the experiment was carried on in duplicate, and the conditions in the different sets were the same except the moisture content. The latter varied from 8 cc. in 1 and 2 to 12 cc. in 9 and 10. The experiment was begun on February 13th and ended on April 11th, when the contents of all the flasks except that of flask 1 were analyzed. In case of No. 1 the contents of the flask were analyzed on March 5th in order to determine whether nitrification was taking place. During the experiments the flasks were kept in the dark and tightly stoppered, so that no loss of water could take place. The nitrites and nitrates were determined by the color methods and the following amounts found:

	No.	Nitrate nitrogen. Mg.	Nitrite nitrogen. Mg.
March 5th	1	1.37	0.0025
April 11th	2	20.00	0.0124
" 11th	3	18.91	0.9100
" 11th	4	18.82	0.4000
" 11th	5	18.82	0.0258
" 11th	6	14.27	4.5710
" 11th	7	15.87	0.0930
" 11th	8	16.65	0.1600
" 11th	9	19.80	2.0151
" 11th	10	19.95	0.0121

The analysis of the soil before nitrification showed it to contain 0.017 per cent. of total nitrogen, 0.00083 per cent. of nitrate nitrogen, and 0.00003 per cent. of nitrite nitrogen. Hence the 100 grams of soil contained, at the beginning of the experiment, 17 mg. of total nitrogen (most of it in fossil remains and practically unavailable for immediate nitrification), 0.83 mg. of nitrate nitrogen, and 0.03 mg. of nitrite nitrogen. To this there were added 100 mg. of ammonium sulphate, containing 21.21 mg. of ammonia nitrogen. It appears, then, that practically all of the ammonia nitrogen was nitrified, and that within the stated limits the different amounts of water affected nitrification but little. Thus from February 13th to March 5th, only 1.37 to 0.83 mg. of nitrate were formed, while from March 5th to April 11th (only thirty-six days), more than 18.5 mg. of ammonia nitrogen were oxidized. Furthermore, the comparatively large amounts of nitrite nitrogen in some cases show that nitrification was still incomplete, or that the nitrates already formed were being reduced again. It will be noticed that in No. 6 where the amount of nitrate nitrogen is the least, the amount of nitrite nitrogen is the greatest, namely, 4.57 mg., an unusually large amount.

On April 30th the soil leachings of this series, that had been kept in stoppered flasks, were again analyzed for nitrates, 100 cc. being taken for each determination as previously. In this case duplicate determinations were made. There was found in :

No.	Duplicate determinations.		Mean Mg.
	Mg.	Mg.	
1	16.80	16.65	16.72
3	18.35	18.72	18.53
4	16.15	16.10	16.12
5	18.52	18.32	18.42
6	12.12	12.25	12.18
7	17.42	17.20	17.31
8	17.30	16.90	17.10
9	15.47	15.62	15.54
10	13.16	13.40	13.28

The liquid in the stoppered flasks remained clear, still it is quite evident that there was a reduction of nitrates between April 11th and April 30th, for in all cases but two (7 and 8) the second analysis showed less nitrates than the first. In 9 and 10 the difference was considerable, and in 5 the difference but slight.

In Series II it was decided to study the effect of sodium chloride on nitrification. One hundred grams of loam from the college farm, containing 201 mg. of total nitrogen and 4 mg. of nitrate nitrogen, were placed in each flask. The latter was kept in the dark and tightly stoppered from February 14th until April 16th. Flask No. 11 cracked when the experiment began, and nitrification in it stopped as soon as the soil became dry. The following is the scheme of the experiment :

Flask.	Ammonium sulphate. Mg.	Water. cc.	Soil extract. cc.	Sodium chloride. Mg.
19	50	11	1	..
20	50	11	1	..
21	50	11	1	10
22	50	11	1	10
23	50	11	1	50
24	50	11	1	50
25	50	11	1	100
11	50	11	1	100

Each flask had also one-half gram of calcium carbonate added to it. When analyzed on April 16th, the following amounts of nitrate and nitrite nitrogen were obtained :

	Nitrate. Mg.	Nitrite. Mg.
19	27.77	0.0154
20	27.82	0.030
21	25.97	0.014
22	25.65	0.015
23	23.88	0.015
24	23.80	0.022
25	22.72	0.030
11	10.67	0.020

As stated above, flask No. 11 was not under the conditions of the experiment, for it lost its moisture long before the experiment was completed. Otherwise the results are uniform, and while there is a distinct diminution in the amount of nitrates produced as the amount of salt is increased, still the differences are not very great, and from this experiment we must conclude that

quantities of salt up to 0.1 per cent. or 3,500 pounds to the acre, while they retard nitrification, do not stop it entirely.

In Series III it was proposed to study the influence of ferrous salts on nitrification, since in low-lying lands these salts occur at times in considerable quantities. Ferrous sulphate was selected for the purpose. As in Series II, 100 grams of loam soil were used, and besides the substances mentioned in the table below each flask had also 0.5 gram of calcium carbonate added to it to furnish enough available base for the free acid formed. Following is the scheme of the experiment :

Flask.	Ammonium sulphate. Mg.	Water. cc.	Soil extract. cc.	Ferrous sulphate. Mg.
12	50	11	1	..
13	50	11	1	10
14 <sup>1</sup>	50	11	1	10
15	50	11	1	50
16	50	11	1	50
17	50	11	1	100
18	50	11	1	100

The experiment began on February 14th and ended on April 14th. The conditions were the same as those in Series II. Flask No. 16 was found to be badly cracked on February 27th and was, therefore, analyzed on that day. On April 14th the following amounts of nitrate and nitrite nitrogen were found.

No.	Nitrate. Mg.	Nitrite. Mg.
12	28.62	0.012
13	33.32	0.020
14	33.32	0.015
15	25.00	0.045
16 <sup>1</sup>	5.00	....
17	25.00	0.023
18	25.00	0.024

There was apparently but little influence of the ferrous salt on nitrification, although the larger quantities used seemed to retard it a little. In the case of flask No. 16 there was scarcely any nitrification in the thirteen days between February 14th and February 27th, which again brings out the fact that the period of incubation lasts for some time.

On May 6th the nitrates were redetermined in Series II, and the following amounts of nitrate nitrogen found :

<sup>1</sup> Analyzed February 27th.

Flask.	Duplicate determinations.		Mean. Mg.
	Mg.	Mg.	
12	27.55	27.82	27.68
13	28.92	29.07	28.99
14	34.45	34.50	34.42
15	29.17	29.22	29.19
16	....	....	....
17	30.87	31.30	31.08
18	34.17	34.01	34.09

The general tendency in this case seems to have been a gain in nitric nitrogen. As it is, the amounts of ferrous sulphate used had not the power to stop nitrification.

In Series V equivalent quantities of calcium carbonate and calcium sulphate were compared as to their influence on nitrification. The scheme of experiment was as follows :

Flask.	Water. cc.	Soil extract. cc.	Ammonium sulphate. Mg.	Calcium carbonate. Grams.
28	13	1	100	0.5
29	13	1	100	0.5
36	13	1	100	1
37	13	1	100	1
38	13	1	100	2
39	13	1	100	2
Calcium sulphate.				
40	13	1	100	0.7555
41	13	1	100	0.7555
42	13	1	100	1.511
43	13	1	100	1.511
44	13	1	100	2.2665
45	13	1	100	2.2665

The experiment lasted from February 20th until April 20th, the conditions being the same as in the other series. It was intended to compare flasks Nos. 28 and 29 with the flasks of this series, since the conditions were the same. The amounts of nitrate and nitrite nitrogen were as follows :

Flask.	Nitrate, duplicate determinations.		Mean. Mg.	Nitrite. Mg.
	Mg.	Mg.		
28	32.77	....	32.77	0.035
29	38.81	....	38.81	0.033
36	27.60	27.92	27.76	0.054
37	42.05	41.72	41.88	0.038
38	31.55	32.07	31.81	0.049
39	20.27	19.90	20.08	0.039
40	19.30	19.55	19.42	0.049
41	18.72	18.72	18.72	0.036
42	16.82	16.82	16.82	0.024
43	19.52	19.98	19.75	0.035
44	20.62	20.35	20.48	0.040
45	18.52	18.22	18.37	0.036



Where equivalent amounts of gypsum were used the nitrification was, on the whole, fairly uniform, and slighter than in the flasks where calcium carbonate was used. The agreement among the latter is not, however, all that might be expected. Thus, for instance, there were only 27.76 mg. of nitrate nitrogen found in flask No. 36, while in flask No. 37, treated in exactly the same way, there were found 41.88 mg. of nitrogen as nitrate. What the difference is due to is difficult to decide with certainty, although in dealing with micro-organisms such striking, and apparently unexplained, differences occur. On May 2nd, flasks Nos. 37 and 38 were again analyzed for nitrates, and the following amounts found.

Flask.	Duplicate determinations.		Mean. Mg.
	Mg.	Mg.	
37	48.07	47.65	47.86
38	36.98	37.04	37.01

In flask No. 37 there was a gain of from 41.88 to 47.86, almost 6 mg.; in flask No. 38 there was a gain of from 31.81 to 37.01 mg., or more than 5 mg. of nitric nitrogen.

In Series VI it was proposed to study the relation of large quantities of organic matter to nitrification. Linseed meal, containing, as analyzed by the Kjeldahl method, 4.51 per cent. of nitrogen, was used for the purpose. The following is the scheme of the experiment:

Flask.	Water. cc.	Soil extract. cc.	Calcium carbonate. Gram.	Linseed meal. Grams.
26	13	1	0.5	..
27	13	1	0.5	..
46	13	1	0.5	0.5
47	13	1	0.5	0.5
48	13	1	0.5	1.0
49	13	1	0.5	1.0
50	13	1	0.5	3.0
51	13	1	0.2	3.0

Flasks Nos. 26 and 27 being carried on under the same conditions as the flasks of Series VI, it was intended to place them also as blanks in Series VI. As reported elsewhere, however, they were cracked at the beginning of the experiment. The experiment in question lasted from February 20th until April 21st. Analyses for nitrate and nitrite nitrogen showed:

flask.	Nitrate, duplicate determinations.		Mean Mg.	Nitrite. Mg.
	Mg.	Mg.		
46	31.42	32.55	31.83	0.046
47	29.52	29.44	29.48	0.053
48	38.57	39.17	38.87	0.051
49	33.70	33.94	33.82	0.071
50	....	....	0.14	0.010
51	....	....	0.0013	0.002

It appears that more nitrate was formed where 1 per cent. of organic matter was present than where only 0.5 per cent. was present. On the other hand, but traces of nitrates were found at the end of the experiment in flasks Nos. 50 and 51, where 3 per cent. of organic matter was used.

### RAPID METHOD FOR THE VOLUMETRIC DETERMINATION OF MOLYBDENUM STEEL.

By FRANCIS T. KOPP.

Received October 4, 1901.

**W** EIGH 0.5 gram of sample in a platinum crucible of about 100 cc. capacity, adding 2 cc. of sulphuric acid (sp. gr. 1.58), and 12 cc. of water. When thoroughly dissolved, which may be assisted by heating, evaporate over the Bunsen burner until white fumes are given off, cool, add 30 grams fused potassium hydrogen sulphate, and gently raise the temperature to a bright heat, holding it at this temperature until the sample is thoroughly fused, which usually will require ten to fifteen minutes.

Care is required in both evaporating and fusing the sample that no particles be carried over the top of the crucible, by the water being driven off too swiftly and thereby causing a spattering, or by fusing too briskly, the gas given off by the potassium hydrogen sulphate either carrying particles away, or causing the fusion to foam over the top.

When thoroughly fused, run the fusion around the side of the crucible and allow to cool. When cold, place the crucible and fusion in a No. 5 beaker containing 500 cc. of *hot* water, and keep it nearly boiling until the fusion is dissolved and the solution has become transparent; then wash the crucible with water into the beaker containing the solution.

Cool the solution to normal temperature and transfer to a liter flask, rinsing the beaker with water, and add 100 cc. ammonia

(sp. gr. 0.90) and make up with water to the liter mark ; transfer the solution back and forth from the flask to a *dry* beaker several times to thoroughly mix.

Allow the precipitate to settle, and filter on a *dry* filter ; take 500 cc. of the filtered solution and add 40 cc. sulphuric acid (sp. gr. 1.58) and run through a zinc reductor which consists of a column of zinc, some 12 inches long and 0.5 inch in diameter (Jones' reductor).

Add 10 cc. sulphuric acid (sp. gr. 1.58) to the reduced solution, and titrate with standard solution of potassium permanganate (1 cc. of potassium permanganate = 0.003053 gram of iron).

A "blank," consisting of 450 cc. water, 50 cc. ammonia (sp. gr. 0.90), and 40 cc. sulphuric acid (sp. gr. 1.58), must be run through the reductor to correct error due to the impurities in the zinc ; add 10 cc. sulphuric acid (sp. gr. 1.58) and titrate with permanganate (standard solution), the number of cubic centimeters used to be subtracted from the reading of the permanganate used to oxidize the molybdenum trioxide solution.

Subtract the "blank" reading from the reading for the molybdenum trioxide solution and multiply by 0.71776, which will give the Mo. The permanganate used must be of such concentration that 1 cc. = 0.003053 gram iron for use in this calculation. The presence of chromium is not determined.

#### TUNGSTEN STEELS.

When tungsten is present, weigh 1 gram of sample into a No. 1 beaker and dissolve in 25 cc. dilute nitric acid (sp. gr. 1.20) and, when violent action has ceased, add 10 cc. strong hydrochloric acid ; when thoroughly dissolved, evaporate on a hot plate to dryness, bake to separate silica, and redissolve in 15 cc. strong hydrochloric acid, which will precipitate the tungsten as tungsten trioxide ; cool and dilute with water to 100 cc., filter on a *dry* filter, and measure 50 cc. of filtered solution (which should be free from tungsten) into a No. 1 beaker and add 10 cc. sulphuric acid (sp. gr. 1.58). Evaporate the solution in the beaker till fumes are given off, transfer the solution from the beaker to a platinum crucible, and rinse the beaker, evaporating the solution in the crucible over a Bunsen burner until fumes are given off, then add 30 grams potassium hydrogen sulphate (fused) and proceed as in ordinary steel.

## FERROMOLYBDENUM.

Weigh 0.5 gram of the sample into a platinum crucible (100 cc. capacity) and dissolve it with 15 cc. strong nitric acid ; when thoroughly dissolved add 2 cc. sulphuric acid (sp. gr. 1.58) and evaporate over a Bunsen burner until fumes are given off. Care must be exercised here that no nitric acid remains in the crucible. Add 30 grams potassium hydrogen sulphate (fused) and proceed as in the case of steel.

The following are some results obtained by the above methods. Three molybdenum steels were made in crucible fires; the molybdenum contents and analyses are as follows :

Steels. No.	Molybdenum added. Per cent.	Molybdenum found. Per cent.
1	5.00	5.040
2	8.00	8.050
3	10.00	10.014

These analyses were made in duplicate.

A ferromolybdenum was also analyzed by Messrs. Booth, Garrett, and Blair, of Philadelphia, Mr. McCreath, of Harrisburg, and myself. Mr. Whitfield, the chemist who made the analysis for Messrs. Booth, Garrett, and Blair, used the sulphide method given in Blair's "Chemical Analysis of Iron," fourth edition. What method Mr. McCreath used I do not know ; I used the method described above.

Messrs. B. G. and B. Per cent.	Mr. McCreath. Per cent.	Volumetric. Per cent.
50.53	50.34	50.45

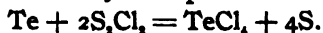
A molybdenum steel containing chromium was analyzed by Mr. McCreath and myself with results as follows : Mr. McCreath, 7.42 ; volumetric, 7.81. A tungsten molybdenum chrome steel was made, the amount of molybdenum added to steel being 3.6 per cent. ; molybdenum found was 3.59 per cent. All of my analyses were made in duplicate.

## TELLURIUM TETRACHLORIDE.

BY VICTOR LENHER.

Received December 27, 1901.

WHEN an excess of sulphur monochloride is brought in contact with metallic tellurium at the ordinary temperature, the tellurium is rapidly attacked, heat is evolved, and in a few moments white needle-like crystals of tellurium tetrachloride separate. The reaction may be represented as follows :



The free sulphur indicated in the reaction dissolves in the excess of sulphur chloride, and on evaporation is shown to be present.

Tellurium tetrachloride is insoluble in sulphur chloride, and in carbon bisulphide. Inasmuch as sulphur chloride dissolves in carbon bisulphide in all proportions, when the latter solvent is brought in contact with a mixture of tellurium tetrachloride, and sulphur chloride containing sulphur in solution, it is only necessary to extract this mixture with carbon bisulphide when the pure crystals of tellurium tetrachloride are obtained. In actually carrying out this preparation, the sulphur chloride is usually decanted from the crystals which are then thoroughly washed with carbon bisulphide.

Tellurium tetrachloride prepared in this manner appears as white needle-like crystals which are almost insoluble in sulphur chloride in the cold, but dissolve readily in the hot reagent.

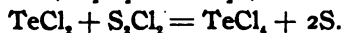
On analysis, 0.5164 gram tellurium tetrachloride gave 0.2430 gram tellurium, or 47.06 per cent. Theory requires 47.21 per cent.

0.2305 gram tellurium tetrachloride gave 0.4863 gram silver chloride, or 52.20 per cent. chlorine. Theory requires 52.79 per cent.

The chloride thus obtained is permanent in dry air, but in moist air decomposes with formation of the oxychloride. Excess of water gives tellurous acid.

When heated with metallic tellurium the black dichloride is formed.

This method of preparing tellurium tetrachloride is frequently very convenient when the pure salt is desired. The reaction of sulphur monochloride on tellurium with formation of the tetrachloride takes place as indicated, at any temperature from the ordinary to  $139^{\circ}$ , the boiling-point of sulphur chloride, when the latter is in excess. An experiment was conducted, heating metallic tellurium to a high temperature in a current of sulphur chloride. The tellurium was placed in a porcelain boat in a combustion tube. When sulphur chloride vapor comes in contact with highly heated tellurium, the black dichloride of tellurium is first formed, but quickly changes into tetrachloride.



In this experiment, beautiful long white needles of tellurium tetrachloride were deposited on the sides of the tube, beyond the

porcelain boat, even while black tellurium dichloride yet remained in the boat.

In studying the replacing action of sulphur, selenium and tellurium, Krafft and Steiner<sup>1</sup> heated 2 parts sulphur chloride with 2.2 parts of tellurium in an open combustion tube. Since they worked with a slight excess of tellurium, the dichloride was obtained, but they do not appear to have observed that with excess of sulphur chloride, the tetrachloride is obtained, the yield being practically quantitative.

UNIVERSITY OF WISCONSIN,  
MADISON, WIS.

## PRELIMINARY COMMUNICATION UPON GLUCOPHOSPHORIC ACID.

By P. A. LEVENE.

Received November 11, 1901.

**P**HOSPHORIC acid is a very important constituent of all living matter. It enters in organic combination with nearly every cell constituent. As glycerophosphoric acid it enters the molecule of lecithin, which is a "primary cell constituent"; in a like manner it combines with proteid, forming the so-called "paranucleic acid." Further, in combination with purin bases it forms the most important cell constituent, known as nucleic acid.

The latter substance, however, is very complex, and its composition is not fully known. At the present stage of our knowledge on the subject it seemed of great importance to analyze the substances related to nucleic acid but of a less complex nature. For this reason I undertook the analysis of a substance first obtained by Palladin<sup>2</sup> from different seeds, and later analyzed by Schulze and Winterstein.<sup>3</sup>

Schulze and Winterstein made an elementary analysis of the substance obtained by Palladin himself, and according to them it contained :

	Per cent.
Carbon .....	9.65
Hydrogen .....	2.83
Phosphorus pentoxide.....	34.66
Ash .....	67.88

In my hands the method of Palladin did not prove very satis-

<sup>1</sup> *Ber. d. chem. Ges.*, 34, 560.

<sup>2</sup> Palladin: *Ztschr. Biol.*, (1894), p. 199.

<sup>3</sup> Schulze and Winterstein: *Ztschr. physiol. Chem.*, 32, 90.

factory and by a comparatively simple method, which I shall describe later, I obtained a copper salt of an acid of the following composition :

0.1380 gram of the substance on combustion gave 0.0858 gram carbon dioxide and 0.0355 gram water ; or 16.95 per cent. carbon and 2.85 per cent. hydrogen.

0.2364 gram of the substance on combustion gave at 723.1 mm. pressure and 14.0°, 6 cc. nitrogen, or 2.41 per cent.

0.1735 gram of the substance, on fusion with sodium hydroxide and potassium nitrate, gave 0.0658 gram magnesium pyrophosphate, or 24.10 per cent. phosphorus pentoxide.

0.0950 gram of the substance gave 0.0548 gram of ash, or 57.67 per cent.

The ash contained 0.0339 gram cupric oxide or 35.66 per cent.

#### SUMMARY.

	Per cent.
Carbon.....	16.95
Hydrogen .....	2.85
Nitrogen.....	2.41
Phosphorus pentoxide.....	24.10
Cupric oxide.....	35.66
Ash.....	57.67

A solution of the salt in nitric acid containing ammonium nitrate gave no reaction for phosphoric acid with ammonium molybdate solution, thus showing that the salt was not contaminated with inorganic phosphates. In the seed the acid is present in the form of its calcium magnesium salt. The latter salt is precipitated by alkalis and by sodium acetate ; it is soluble in dilute acids. A comparatively dilute acetic acid solution of it added to an acid solution of Witte's peptone forms a precipitate. On hydrolysis of the substance with dilute mineral acids it yielded orthophosphoric acid ; no glycerol could be extracted, nor any appreciable quantity of fatty acids. Also the purin bases were not detected among the decomposition products. The free acid obtained from the copper salt did not give the slightest biuret test. However, the solution of the copper salt in hydrochloric acid heated over a flame was capable of reducing Fehling's solution.

With phenylhydrazine the products of hydrolysis formed a crystalline deposit characteristic for glucosazones. It is thus suggestive that a carbohydrate enters the molecule of this organic phosphoric acid.

A further study on the composition of the substance is in progress.

## NEW BOOKS.

**ANALYSE DES ENGRAIS.** BY D. SIDERSKY. Paris: Published by C. Beranger. 240 pp.

This little work of 240 pages was written by D. Sidersky, chemical engineer and officer of the *Mérite Agricole*, and one of the leading members of the *Association des Chimistes de Sucrierie et de Distillerie de France et des Colonies*.

The immediate cause of the preparation of the book was a resolution, proposed by M. Déhéraïn, and adopted at the Second International Congress of Applied Chemistry, held at Paris in 1896, to the following effect: that the different official methods for the analysis of fertilizers be collected into one publication in the French language, and that M. Sidersky be charged with this publication.

In the discharge of this office, M. Sidersky was met with a number of difficulties. Certain countries were modifying their systems and without bringing them into concordance with neighboring countries; for instance, Holland, Belgium and the Grand Duchy of Luxembourg. Switzerland had also just changed her own methods and adopted those of Germany, while in Germany even the publication of the official methods was long delayed. Meanwhile, the Third International Congress of Applied Chemistry, held in Vienna in 1898, appointed an international committee which was charged with a study of the best methods of the analysis of fertilizers and fodders, with the object of opening the way for international agreement. M. Sidersky, as well as the writer, was made a member of this commission, and the preparation of his volume was delayed until this commission reported the results of its work. This took place at the fourth congress in Paris, in 1900, where a broad basis was laid for international agreement, without entering into the details thereof. M. Sidersky has, therefore, included in his work the official methods in vogue in the countries named below, and also has included the report of the international committee, adopted at Paris, 1900. The countries whose methods are given in the report are France, Belgium, Holland, Grand Duchy of Luxembourg, Switzerland, Austria-Hungary, United States of America, Italy, and finally the data of the international commission.



In most cases a short historical sketch of the development of the official method is prefixed.

In the preparation of this report M. Sidersky had the collaboration of chemists in the different countries, and he expresses his particular thanks to Maercker and von Grueber, of Germany, Strohmer, of Austria, Peterman, of Belgium, Masson, of Belgium, Hoogewerff, of Holland, Menozzi, of Italy, Dusserre, of Switzerland, and Wiley, of the United States.

The French methods are those still in official use and adopted by the decree of the Minister of Agriculture, in May, 1897.

The methods of Belgium, Holland, and the Grand Duchy of Luxembourg are the same and, in their present form, were adopted by a commission which met at Goes, in January, 1899.

The German methods are those adopted by the Union of the German Agricultural Experiment Stations, revised up to 1898. These methods were adopted by Switzerland on the 27th of July, 1897.

The methods for Austria-Hungary were adopted at a meeting of the agricultural experiment stations of Austria-Hungary, held in Vienna the first of April, 1897.

The methods for the United States are those adopted by the Association of Official Agricultural Chemists, in September, 1895. Very few changes have been introduced in the official methods in use in this country since that time, but still some rather important ones should have been noted by the author, to whom the latest methods were sent.

No date is given for the Italian official methods, but they are published as written by Prof. Menozzi.

The methods of the international commission are those adopted at the Fourth International Congress, at Paris, in 1900.

There is no space here to enter into details of the methods in the book, except to commend the publication of these international methods in full in a convenient form for comparison. It may be said that the methods for fertilizers are now so well established that it should be entirely possible for an international method to be adopted which would be followed not only by official chemists, but all other chemists studying fertilizer materials throughout the world. A comparison of the various official methods given shows a basic agreement on principles of analysis.

A study of the different methods, however, reveals a great

difference in details. This difference, however, the international commission sought to eliminate as much as possible by the establishment of the basic principles on which the analyses should be conducted, and a reference to the various official methods for the details in each case.

This work points out in a most marked manner the functions still remaining to the international commission; *viz.*, to secure at least practical unity in details of manipulation, as well as in the principles of the analysis. M. Sidersky is to be congratulated on the effective manner in which he has carried out the instructions given him by the International Congress.

H. W. WILEY.

A SHORT MANUAL OF INORGANIC CHEMISTRY. BY A. DUPRÉ, PH.D., AND H. WILSON HAKE, PH.D. Third edition, revised and partly rewritten with special reference to the periodic law. London: Charles Griffin & Company; Philadelphia: J. B. Lippincott Company. 1901. ix + 391 pp. Price, \$3.00.

The introductory portion which precedes the description of the properties of the various elements and their compounds is very concise, and needs must be so to condense within the space of 101 pages all the general principles of chemistry, together with much information on physical and thermo-chemistry.

In Chapter VI the authors say in a foot-note: "A rapid method, not commonly known, for converting centigrade degrees into Fahrenheit degrees, is as follows: double the centigrade degrees, and subtract from them one-tenth of their quantity; to the remainder add 32, and the result is the corresponding degrees Fahrenheit."

This method while not new is very rapid, and deserves to become more widely known.

Some "Typical Elements and their Compounds" are then considered, 96 pages being devoted to oxygen, hydrogen, nitrogen, carbon, boron, silicon, sulphur, and phosphorus. The remainder of the elements are then treated according to the periodic system of classification.

The scheme followed in discussing the properties of the elements and their compounds is as follows: name; symbol and atomic weight; formula; molecular weight and percentage composition; occurrence in nature; physical properties; chemical properties; distinguishing tests; physiological action; preparation or manufacture; application; historical matter.

Under the heading "Physiological Action," it would have been well had the authors adhered to the original idea somewhat more closely. For example, under PH, nothing is said in reference to its poisonous character; again, sodium phosphate and potassium nitrate are not referred to as having any physiological action, while zinc sulphate, which is largely used as a mild astringent, is only mentioned as an emetic.

On the whole the work is clearly and concisely written, and contains a vast amount of information in a comparatively small space.

The book is poorly bound, many of the leaves separating entirely from the volume during the reading for review.

J. A. MILLER.

CHEMICAL LECTURE EXPERIMENTS. BY FRANCIS GANO BENEDICT, PH.D.  
New York: The Macmillan Co. 1901. xiii + 436 pp. Price, \$2.00.

Dr. Benedict's purpose in preparing this book is, as he says, "primarily to furnish teachers with a large number of reliable lecture experiments." His aim is, also, to suggest experiments that may be performed with an ordinary laboratory equipment. Although excellent manuals of this kind have been prepared in this country, in Germany and in England, no one will, I think, consider this book of Dr. Benedict superfluous. The experiments are so well chosen and so clearly described with so many valuable and practical hints, that even a novice should have no difficulty in making them successfully. The omission of many experiments requiring fragile or costly apparatus may cause some regret, but since descriptions of most of them are to be obtained from the text-books that will probably be found in nearly all school or college libraries, their exclusion does not detract seriously from the value of the book.

The greater portion of the text is devoted to the illustration of the properties of the non-metals, but some very interesting experiments on the metals and their compounds are described. Any teacher will, I think, find this work a useful addition to his library.

L. B. HALL.

RESEARCH PAPERS FROM THE KENT CHEMICAL LABORATORY OF YALE UNIVERSITY. EDITED BY F. A. GOOCH. In two volumes. 8vo. Vol. I, xvi + 411 pp. Vol. II, xii + 415 pp., with 20 figures in the text. New York: Chas. Scribner's Sons. Price, \$7.50.

These papers are reprinted chiefly from the *American Journal*

*of Science* in honor of the Bicentennial of Yale University. The mechanical execution of the volumes is superb. A large majority of the papers are by Professor Gooch himself and it is probable that he was more or less concerned with others where his name does not appear. Yale University and Professor Gooch may well feel proud of the amount and quality of the work carried to completion in this laboratory during the time covered by these volumes. The subjects treated are mostly in analytical chemistry, to which these papers are a most substantial contribution.

E. H.

AMERICAN HANDY-BOOK OF THE BREWING, MALTING, AND AUXILIARY TRADES. BY ROBERT WAHL AND MAX HENIUS. Chicago: The authors, 294 S. Water Street.  $6\frac{1}{2} \times 4\frac{1}{4}$  inches; xvi + 1266 pp. Copiously illustrated. Price, \$10.00.

The chapter headings will give an idea of the contents. They are: Arithmetic; Algebra; Mensuration; Weights and Measures; Physics; Mechanics; Elements of Machinery; Power; Transmission of Power; Steam Engines; Refrigeration; Pumps; Brewery Buildings; Chemistry; Brewing Materials; Micro-organisms; Yeasts and Fermentation; Pure Yeast Culture; Malt House Outfit; Malting Operations; Brewery Outfit; Brewery Operations; The Bottling Department of a Modern Brewery; Figuring in the Brewery; The Brewers' Chemical Laboratory; The Brewers' Microscopical Laboratory; Lubricants and Lubrication; Legal Relations of the Brewer Beer Dietetics and Economics; Miscellaneous Information; Bibliography; Dictionary of Technical Terms; Publications Consulted; Index.

The book will be of use to others than brewers. The information given seems to be full and accurate, and shows evidence of great care in preparation. The mechanical execution—printing, binding, illustrations—is excellent.

E. H.

HANDBOOK ON SANITATION. A Manual of Theoretical and Practical Sanitation. For Students and Physicians; for Health, Sanitary, Tenement-house, Plumbing, Factory, Food, and other Inspectors, as well as for Candidates for all Municipal Sanitary Positions. BY GEORGE M. PRICE, M.D., Medical Sanitary Inspector, Department of Health, New York City, etc. New York: John Wiley & Sons. 1901. xii + 317 pp. Price, \$1.50.

This little handbook covers a large field very briefly and in very simple language. The first part is devoted to a brief discussion of the principal topics in sanitary science. Exception

must be taken to the positive statements with regard to certain of the diseases which are said to be traceable to soil influences because recent investigations in sanitary science have demonstrated conclusively that most of these diseases arise independently of soil conditions. The same criticism must be made with regard to the statements respecting the detrimental influence upon health of the sewer air.

The portion of the book treating of the duties and operations of the sanitary inspector will be of special service to those qualifying for such positions.

The use of the word "sanitation" to designate the profession of sanitary inspector is not to be commended as it is confusing and misleading because sanitation is not a profession.

In part four of the book are given the different sanitary laws of the state and city of New York under which tenement-houses, plumbing, drainage, and ventilation of buildings, schools, and milk are inspected, as well as the regulations governing the disinfection of tenements and buildings in infectious diseases.

D. H. BERGEY.

LEITFADEN FÜR DEN UNTERRICHT IN DER ANORGANISCHEN CHEMIE. Zweiter Teil. BY DR. JOACHIM SPERBER. Zurich: Verlag von E. Speidel. 1901. 163 pp.

This book is the second part of the volume bearing the same title which was reviewed in this Journal, 22, 222. This volume treats entirely of the oxygen acids of the various elements, giving a detailed description of the methods of preparation of the oxides and the corresponding acids, and a full description of the properties of each. The commercial manufacture of sulphuric acid is treated in great detail, but the more recent contact process is not mentioned. The recently developed electrolytic processes for the manufacture of chlorates, alkali, and bleaching-powder are described satisfactorily.

In the opinion of the reviewer the author has erred in introducing too great a degree the structural formulas which are used throughout the book. Particularly is this the case with the sodium-potassium sulphite, which the author uses to introduce the subject of isomerism, especially so since the recent work of Fraps seems to throw considerable doubt on the existence of isomeric salts of sulphurous acid.

HENRY FAY.

**SUBJECT LIST OF WORKS ON CHEMISTRY AND CHEMICAL TECHNOLOGY,** in the Library of the British Patent Office, being No. 6 of the Library Series, and No. 3 of the Bibliographical Series. London. 12mo. 105 pp. 1901. Price, 6 d.

The book is arranged in two parts, first a general alphabet of subject headings, with descriptive entries in chronological order, of the works arranged under those headings, and second a key, or summary of headings shown in class order. The catalogue comprises 885 works, of which 79 are serials, and represents 3,300 volumes. The chronological arrangement is very useful for the purposes of a patent office library, as it enables a searcher to see at once the date and consequent probable value of a book on his subject. Among the early works we notice 10 books on mines and mining called "Pirotechnia," by V. Biringuccio, 1558-9; and the "Works" of J. R. Glauber, containing a "great variety of choice secrets in medicine and alchemy" 1689; also R. Boyle, "The Sceptical Chymist," 1661; etc.

The principal or leading headings of classification are alchemy, analysis, biography, technology, chemical dictionaries, periodicals and digests, inorganic, metalloids, metals, organic, physical, and theoretical, and practical chemistry which covers laboratories, apparatus, and chemical optics, and includes catalogues.

It may be not generally known that the U. S. Patent Office at Washington contains one of the best technical libraries in this country, open to the public for consultation.

WM. H. SEAMAN.

**SMOKELESS POWDER, NITROCELLULOSE, AND THE THEORY OF THE CELLULOSE MOLECULE.** BY JOHN B. BERNADOU. Lieutenant U. S. Navy. New York: John Wiley & Sons. 1901. Small 8vo. viii + 200 pp. Price, \$2.50.

Under the first legend there are 38 pages of a lecture by Bernadou, on the "Development of Smokeless Powder," reprinted from the *Proceedings of the U. S. Naval Institute* and 30 pages of a translation of a paper by Mendeléeff on "Pyrocellulose Smokeless Powder," though the source from which the latter is taken is omitted. Under the second legend there are 47 pages given to translations of the papers of Vieille and of Bruley on the "Nitration of Cotton." The only newly presented matter is embraced in the first 80 pages and here the author develops his "Theory of the Cellulose Molecule," after treating of the "Earlier Views as to Nitrocellulose Composition and Constitution," The Concep-

tion of Progression in Relation to Composition and Constitution," and of "Solutions of Nitrocellulose."

In his lecture Bernadou bases his argument for the proper composition of a powder on the relative volumes of carbon dioxide and of carbon monoxide produced from the same mass of carbon when burned with oxygen, but in making this elementary calculation he uses 1.9 (which is approximately the weight in grams of a liter of carbon dioxide at normal) as the specific gravity of carbon dioxide, and 1.4 (which is practically 0.1 of the relative density of carbon monoxide) as the specific gravity of carbon monoxide.

His essay on the "Theory of the Cellulose Molecule," is of the most speculative character and the pages bristle with curious graphic formulas which are arranged in purely fanciful ways and from which he draws the most sweeping generalizations regarding the upbuilding of cells, the characteristics of organic life, and the like. He is unhampered by conventions and since, for instance, the accepted formula for ethyl hydroxide does not serve his convenience he assigns to this substance a "strain" formula in which the atoms are arranged as in the accepted formula for dimethyl oxide. He seems to regard linkages as matters of slight consequence and having assumed, without giving any evidence, the existence of median double linkages in the cellulose molecule, he shifts them to terminal single bonds at will, since, as he states, the molecule "may be expressed" in this way "without radical modification."

The book bears throughout evidence of the ambitious amateur, and one wonders how a man dares risk his reputation in his own profession by excursions into other professional fields of work where his deficiencies become apparent. The pursuit of one's own profession ought to furnish opportunities to satisfy any laudable ambition.

CHARLES E. MUNROE.

**A COMPENDIUM OF GOLD METALLURGY AND DIGEST OF U. S. MINING LAWS, WATER RIGHTS AND DESERT LAND LAWS.** By E. M. and M. L. WADE. Published by the authors, Los Angeles, Cal. 140 pp. Second Edition. Price, \$1.00.

The book, as stated in the introduction, is intended for the mining public which has little or no knowledge of metallurgy, and appearing now in a second enlarged edition seems to have filled a certain want. It is divided into eight chapters and has

five appendices. In the first part are found brief discussions of the characteristics of gold and quicksilver, and of ores and country rock; further outlines are given of the processes of amalgamating, concentrating, leaching, and smelting. In the second part there are articles on the occurrence and prospecting of gold ores, and on the methods of sampling, assaying, and testing.

The authors who, according to the illustrated advertisements contained in the book, are in charge of ore-testing works and of laboratories for assaying and analyzing, show in the text that they have a practical knowledge at least of the milling of gold ores and of the current assay methods. Many valuable hints are given which will be of interest to any reader. The general non-chemical mining public, however, will find that more chemical knowledge has been presupposed than can be picked up at random. The book will be of service to a foreman who knows the practical details of his work and wishes to have some sort of elementary primer to help him along. Presupposing that the matter contained in the book is well chosen, a more logical arrangement would be of much benefit.

H. O. HOFMAN.

---

### BOOKS RECEIVED.

**Handbook on Sanitation.** A handbook of theoretical and practical sanitation. By George M. Price, M.D. New York: John Wiley & Sons. 1901. xii + 317 pp. Price, \$1.50.

**The Manufacture of Alum and the Sulphates and Other Salts of Alumina and Iron; Their Uses and Applications as Mordants in Dyeing and Calico Printing, and Their Other Applications in the Arts, Manufactures, Sanitary Engineering, Agriculture and Horticulture.** By Lucien Geschwind. Translated from the French by Chas. Salter, with 195 illustrations. 1901. London: Scott, Greenwood & Co.; New York: D. Van Nostrand Co. xii + 387 pp. Price, \$5.00.

**A Laboratory Guide to the Study of Qualitative Analysis.** By E. H. S. Bailey, Ph.D., and Hamilton P. Cady, A.B. Fourth Edition. Philadelphia: P. Blakiston's Son & Co. 1901. 234 pp. Price, \$1.25.

**The Dyeing of Cotton Fabrics.** A practical handbook for the dyer and student. By Franklin Beech. Illustrated by forty-four engravings. London: Scott, Greenwood & Co.; New York: D. Van Nostrand Co. 1901. viii + 282 pp. Price, \$3.00.

**A Report upon Some Factors Relating to the Cane Sugar Industry of Australia.** By Dr. Walter Maxwell. 1901. 16 pp. 4to. Price, 7d.



# THE JOURNAL

OF THE

# AMERICAN CHEMICAL SOCIETY.

---

## NINTH ANNUAL REPORT OF THE COMMITTEE ON ATOMIC WEIGHTS. DETERMINATIONS PUBLISHED IN 1902.

BY F. W. CLARKE.

Received January 6, 1902.

THE year 1901 has not been very prolific in researches upon atomic weights, at least so far as actual publications would seem to indicate. A fair amount of work, however, is announced from various sources, and doubtless it will appear in print during 1902. The investigations of current date are summarized in the following pages :

### NITROGEN.

Scott<sup>1</sup> has carefully redetermined the ratios between ammonium bromide and silver. The silver was purified by various methods, and each experiment is cited with the proper details upon this point. The ammonium bromide was prepared from hydrobromic acid, with ammonia from different sources. It was brilliantly white, and remained so upon heating to 180°, whereas that used by Stas in his investigations became grayish. All weights were reduced to a vacuum, and calculations were made with  $Ag = 107.93$ . Results as follows, but for details the original paper should be consulted :

<sup>1</sup> *J. Chem. Soc.*, 79, 147 (1901).

Weight $\text{NH}_4\text{Br}$ .	Weight Ag.	Molecular weight $\text{NH}_4\text{Br}$ .
4.89631	5.39380	97.975
2.45925	2.70914	97.972
3.29478	3.62928	97.982
4.46957	4.92273	97.994
4.20661	4.63303	97.996
4.23664	4.66644	97.989
4.31464	4.75175	98.001
6.19233	6.82047	97.990
8.77664	9.66608	97.999
10.47233	11.53416	97.994
4.91997	5.41834	98.0028
5.00442	5.51164	97.997
5.17914	5.70390	98.000
4.84099	5.33177	97.995
5.10677	5.62515	97.984

Rejecting the first three experiments, in which the bromide was slightly acid, Scott's mean value for the molecular weight of  $\text{NH}_4\text{Br}$  is 97.995. Stas found 98.032, and Scott supposes that his salt may have contained traces of platinum, whence the grayness which appeared on heating.

As a further check on the determinations Scott collected and weighed the silver bromide produced, and so determined anew the ratio between Ag and AgBr. Data as follows:

Weight Ag.	Weight AgBr.	Ratio AgBr to 100 Ag.
6.82315	11.87733	174.074
9.66809	16.82816	174.059 <sup>1</sup>
5.41906	9.43315	174.0735
5.51258	9.59596	174.074
5.70686	9.93346	174.062
5.33191	9.28093	174.064
5.62572	9.79254	174.067

Stas' value for this ratio is 174.080.

Two additional experiments were made upon the ratio between ammonium chloride and silver.

Weight $\text{NH}_4\text{Cl}$ .	Weight Ag.	Molecular weight $\text{NH}_4\text{Cl}$ .
4.78257	9.64484	53.519
5.51744	11.12810	53.513

In still another experiment connected with these two, the silver chloride was weighed. 4.7850  $\text{NH}_4\text{Cl}$  gave 12.82048  $\text{AgCl}$ . Hence  $\text{NH}_4\text{Cl} = 53.5164$ . Stas' value is 53.532. Further investigations are promised; but until they are complete Scott re-

<sup>1</sup> 174.090 when corrected for a known impurity.

gards it as premature to compute the atomic weight of nitrogen from these data. As they stand they give :

From the bromide,  $\text{NH}_4 = 18.040$ .

From the chloride,  $\text{NH}_4 = 18.059$ .

#### CALCIUM.

The atomic weight of calcium has been redetermined by Hinrichsen.<sup>1</sup> The purest Iceland spar was ignited, and the ratio so determined between  $\text{CaCO}_3$  and  $\text{CaO}$ . A correction is applied for 0.032 per cent. of  $\text{Fe}_2\text{O}_3$ , found by analysis, and assumed to represent  $\text{FeCO}_3$ , in the original mineral. Weights were reduced to a vacuum, and calculations were made with  $\text{O} = 16$ , and  $\text{C} = 12$ . The data are as follows, all corrections applied :

Weight $\text{CaCO}_3$ .	Weight $\text{CaO}$ .	Atomic weight $\text{Ca}$ .
30.72157	17.22354	40.144
32.77791	18.37587	40.141
34.45625	19.31698	40.142
33.36885	18.70723	40.141
Sum, 131.32458	73.62462	40.142

Herzfeld's determinations of the atomic weight of calcium, cited in the report of last year, have been reproduced in the *Berichte*,<sup>2</sup> and so made accessible to the general reader.

#### ARSENIC.

Somewhat elaborate determinations of the atomic weight of arsenic have been made by Ebaugh<sup>3</sup> under the guidance of Edgar F. Smith. First, silver arsenate was converted into silver chloride by heating in hydrochloric acid gas. All weights were reduced to a vacuum. The results are as follows, with  $\text{O} = 16$ ,  $\text{Cl} = 35.45$ , and  $\text{Ag} = 107.92$ .

Weight $\text{Ag}_3\text{AsO}_4$ .	Weight $\text{AgCl}$ .	Atomic weight $\text{As}$ .
0.23182	0.21547	74.987
0.47996	0.44615	74.944
0.52521	0.48820	74.956
0.80173	0.74517	74.996
0.94782	0.88083	75.061
1.02047	0.94830	75.083
1.03558	0.96258	74.974
1.05462	0.98014	75.033

Mean, 75.004

<sup>1</sup> *Ztschr. phys. Chem.*, 39, 311.

<sup>2</sup> Vol. 34, p. 559.

<sup>3</sup> Doctoral thesis, University of Pennsylvania, 1901.

The silver chloride from seven of these experiments was next reduced by heating in hydrogen. The silver contained in the arsenate was thus determined, giving the following data :

Weight $\text{Ag}_3\text{AsO}_4$ .	Weight Ag.	Atomic weight As.
0.23182	0.162175	75.027
0.47996	0.33583	74.950
0.52521	0.367525	74.907
0.80173	0.56099	74.936
0.94782	0.66318	74.959
1.02047	0.71400	74.964
1.05462	0.73771	75.082

Mean, 74.975

Experiments upon the conversion of silver arsenate into bromide were unsatisfactory. The conversion of lead arsenate into lead chloride gave good results, however, as follows : Calculated with  $\text{Pb} = 206.92$ .

Weight $\text{Pb}_3\text{As}_2\text{O}_8$ .	Weight $\text{PbCl}_2$ .	Atomic weight As.
0.38152	0.35381	74.988
0.436197	0.40449	75.016
0.57218	0.53065	74.964
0.60085	0.55717	75.020
0.74123	0.68736	75.010
0.77107	0.71494	75.067
0.88282	0.81858	75.054
0.97779	0.90674	75.054

Mean, 75.022

Three more determinations, based upon the conversion of lead arsenate into lead bromide by heating in gaseous hydrobromic acid, were also successful. Calculated with  $\text{Br} = 79.95$ .

Weight $\text{Pb}_3\text{As}_2\text{O}_8$ .	Weight $\text{PbBr}_2$ .	Atomic weight As.
0.59704	0.73092	75.066
0.61712	0.75567	74.967
0.65799	0.80569	74.980

Mean, 75.004

The general mean of all twenty-six determinations is

$\text{As} = 75.008$ .

Various other methods of determination were attempted, but unsuccessfully.

#### ANTIMONY.

Friend and Smith<sup>1</sup> have applied a new method to the deter-

<sup>1</sup> This Journal, 23, 502 (1901).

mination of the atomic weight of antimony. Potassium tartryl-antimonite (tartar emetic), was heated in dry hydrochloric acid gas, the final residue of the operation being potassium chloride. All weights were reduced to a vacuum. The results were as follows, when  $H = 1.008$ ,  $C = 12$ ,  $K = 39.11$ , and  $Cl = 35.45$ .

Weight of salt.	Weight KCl.	Atomic weight Sb.
1.19481	0.27539	120.345
1.57004	0.36186	120.359
2.00912	0.46307	120.351
2.04253	0.47073	120.379
2.16646	0.49935	120.341
2.25558	0.51982	120.385
2.61255	0.602155	120.350
2.95272	0.68064	120.311

Mean, 120.353

This value approximates to those found by Schneider and by Cooke from their studies of antimony trisulphide.

#### TELLURIUM.

An interesting contribution to our knowledge of tellurium is due to Steiner,<sup>1</sup> who has measured its atomic weight by partial analyses of diphenyl telluride. In this compound, by combustion, the carbon was determined, and from that determination the atomic weight of the metal was computed. The data, for two separate fractions of material, are as follows:

	Weight $C_{12}H_{10}Te$ .	Weight $CO_2$ .	Per cent. C.	Atomic weight.
1.	0.2295	0.5512	51.39	126.1
	0.2559	0.4811	51.28	126.7
	0.23065	0.4341	51.34	126.4
2.	0.2140	0.4031	51.38	126.2
	0.2578	0.4849	51.31	126.6

Mean, 126.4

Calculated with  $C = 12.003$ ,  $H = 1.008$ . The results are, of course, only approximate, and are intended by the author as an indication of a promising method, and as evidence that the atomic weight of tellurium falls below that of iodine, as demanded by the periodic law.

Steiner also gives two analyses of diphenyl selenide, with determinations of the atomic weight of selenium based upon them. The data are:

<sup>1</sup> *Ber. d. chem. Ges.*, 34, 570.

Weight $C_{12}H_{10}Se$ .	Weight $CO_2$ .	Per cent. C.	Atomic weight.
0.2812	0.6375	61.85	78.8
0.5371	1.2158	61.71	79.3

Another communication upon the atomic weight of tellurium is by Pellini<sup>1</sup>, who employed the old methods of oxidation and reduction connecting Te with  $TeO_2$ . His material, however, was purified by means of two organic compounds, diphenyl telluride and diphenyl tellurium dibromide, from which the metal used in the determinations was finally obtained.

First, Te was oxidized to  $TeO_2$  by means of nitric acid. In the first three determinations the dioxide was heated to  $400^\circ$ ; in the remaining four it was fused. The sixth experiment is only partially stated; the figures in the third and fourth columns have been computed by your committee. The final mean result ( $O = 16$ ) is that given by Pellini.

Weight Te.	Weight $TeO_2$ .	Per cent. Te in $TeO_2$ .	Atomic weight.
1.0679	1.3353	79.968	127.70
1.5469	1.9354	79.926	127.41
2.2386	2.7980	80.007	128.05
2.4522	3.0665	79.967	127.73
2.0977	2.6239	79.945	127.56
2.0442	2.5575	79.929	127.43
2.0434	2.5556	79.957	127.66

Mean, 127.65

The reduction experiments performed in hydrogen by Standenmayer's method were only three in number, as follows:

Weight $TeO_2$ .	Loss of weight.	Per cent. Te in $TeO_2$ .	Atomic weight.
1.4680	0.2944	79.945	127.56
1.9968	0.3993	80.000	128.02
1.9575	0.3932	79.913	127.30

Mean, 127.62

The figures obtained are not remarkably concordant, but they tend to confirm the older determinations, and to place tellurium above iodine.

Still a third memoir upon this atomic weight is due to Koethner,<sup>2</sup> whose work is more than ordinarily elaborate and thorough. His material was scrupulously purified, and studied spectroscopically; and the only (minute) impurities which seem to be possibly present are such as would tend to lower the observed atomic

<sup>1</sup> *Ber. d. chem. Ges.*, 34, 3807.

<sup>2</sup> *Ann. Chem. (Liebig)*, 319, 1.

weight. Several methods of determination were attempted, but the final results rest upon the study of the basic tellurium nitrate,  $\text{Te}_2\text{O}_5 \cdot \text{NO}_3 \cdot \text{OH}$ . This salt, on heating under proper precautions, is reduced to  $\text{TeO}_2$ . In the second series of determinations, as given below, the tellurium which served as the starting-point had been distilled *in vacuo*; in the first series that precaution was not taken. The weights were not reduced to a vacuum, and the calculations were based upon  $\text{O} = 15.88$ ,  $\text{N} = 14.93$ , and  $\text{H} = 1$ .

#### SERIES I.

Weight of salt.	Weight $\text{TeO}_2$ .	Atomic weight Te.
2.9373	2.4522	126.39
2.7982	2.3361	126.40
2.8554	2.3840	126.46

Mean, 126.41

If  $\text{O} = 16$ ,  $\text{Te} = 127.36$

#### SERIES II.

Weight of salt.	Weight $\text{TeO}_2$ .	Atomic weight Te.
5.30270	4.42824	126.67
6.00600	5.01543	126.64
5.58039	4.65990	126.62
28.66904	23.94259	126.73
2.83859	3.20560	126.71
5.85449	4.88930	126.69
25.65029	21.42146	126.70

Mean, 126.68

If  $\text{O} = 16$ ,  $\text{Te} = 127.63$

These last values are essentially identical with those found by Pellini. The memoir contains criticisms of the recent work of others upon the atomic weight of tellurium, and is unusually complete.

#### TUNGSTEN.

Taylor<sup>1</sup>, working under the direction of Edgar F. Smith, has made numerous experiments upon the reduction of  $\text{WO}_3$  to  $\text{W}$ , and the reverse oxidation, and has obtained discordant data as to the atomic weight of tungsten. His material was prepared from wolfram, and purified by recrystallization as ammonium tungstate. The discrepancies are probably to be explained by the presence in the latter salt of small quantities of an ammonium-iron-manganese tungstate. Experiments were also carried out

<sup>1</sup> Doctoral thesis, University of Pennsylvania, 1901.

upon the expulsion of  $\text{CO}_2$  from  $\text{Na}_2\text{CO}_3$  during solution in the latter of  $\text{WO}_3$ . This work was done somewhat imperfectly, and the results are not of absolute value; they are, however, encouraging, and show that the method has some presumptive merit. The thesis is essentially a study of methods, rather than of actual determinations of atomic weight. It has value, as showing some of the errors which have vitiated former work, and which may now be avoided.

#### URANIUM.

Aloy<sup>1</sup> has determined the atomic weight of uranium by a new method, which he proposes to apply to other metals as well. The pure nitrate, of unknown weight, was the material studied. Nitrogen was determined volumetrically, and in the same sample the metal was estimated as  $\text{UO}_2$ . From the ratio between these measurements the desired atomic weight was computed. The data given are as follows:

No.	Volume of N. cc.	Atomic weight U.
1	15.25	239.3
2	33.5	239.4
3	38.0	239.6
4	52.5	239.5
5	81.25	239.4
6	125.0	239.5
7	151.2	239.4
8	165.0	239.4

The value finally adopted was  $\text{U} = 239.4$  when  $\text{N} = 14.04$ . The weights of  $\text{UO}_2$  obtained are not published in the paper, so that the accuracy of the work cannot well be estimated. Data of this kind, which cannot be recomputed by the reader, are of very little value. It is to be hoped that the paper is only a preliminary statement, and that the full details of the research will appear later.

#### LANTHANUM.

Brauner and Pavlicek,<sup>2</sup> in determining the atomic weight of lanthanum by synthesis of the sulphate from the oxide, find that the sulphate is always contaminated by Wyruboff's acid sulphate to a notable extent. The latter salt is so stable that even at  $500^\circ$  some of it remains undecomposed, while another portion

<sup>1</sup> *Compt. rend.*, 132, 351; also, more fully, in *Ann. chim. Phys.*, (7), 24, 418.

<sup>2</sup> *Proc. Chem. Soc.*, 17, 63.



of sulphate in the same crucible may have been reduced to a basic compound. Hence all "equivalent" determinations of rare earths hitherto made by the sulphate method are vitiated by this error. Applying, by actual measurement, the necessary correction for excess of acid, and also correcting for the absorption of hygroscopic moisture by lanthanum sulphate, the authors find for the atomic weight of the metal in the most positive fraction of their material, the value  $L_a = 139.0$ . Ordinary lanthanum, however, the authors regard as a complex of this true lanthanum with another earth metal.

#### PRASEODYMIUM.

Brauner<sup>1</sup> determines the atomic weight of this metal by four methods. First, by analysis of the anhydrous sulphate, whence  $Pr = 140.95$ . Second by the analysis of the oxalate, whence  $Pr = 140.95$ . Third, by synthesis of the sulphate from the oxide, which gave  $Pr = 140.78$ . Fourth, a series like the third, but with corrections for the presence of acid sulphate and hygroscopic moisture, gave  $Pr = 140.93$ . The mean result adopted is  $Pr = 140.94$ . Detailed weighings are not given. An ebullioscopic determination of the molecular weight of praseodymium chloride confirmed the foregoing value.

#### NEODYMIUM.

Also determined by Brauner<sup>1</sup> by means of the sulphate method. Result, corrected for the presence of acid sulphate,  $Nd = 143.80$ .

#### THORIUM.

By the hydrolysis of thorium oxalate Brauner<sup>1</sup> claims to have decomposed commercial thoria into two earths which he calls  $Th_a$  and  $Th_b$ . For thorium alpha the atomic weight determinations by the oxalate method gave 233.5, and by the sulphate method 233.3 to 233.7. The most negative fractions of his material, the thorium beta, first gave the value 232.5, which, by further purification, was reduced to 232 and 231.9. By continued fractionation an oxide was obtained, giving an atomic weight of  $Th_b = 220$ . This decrease was accompanied by a reduction in the density of the oxide from 10.2 to 9.6. The complex nature of the thorium heretofore known may therefore be regarded as proved.

<sup>1</sup> *Proc. Chem. Soc.*, 17, 65.

<sup>2</sup> *Ibid.*, 17, 66.

<sup>3</sup> *Ibid.*, 17, 68.

Similar results to those announced by Brauner, were independently and almost simultaneously obtained by Baskerville.<sup>1</sup> Oxides were prepared, ranging in specific gravity from 8.47 to 11.26, the most definite or real thorium oxide giving values from 9.188 to 9.253. The lowest figures represent an oxide which occurs in small amount in ordinary thoria, the higher to a new earth. The purest thorium compound prepared was a tetrachloride, upon which atomic weight determinations were made,  $\text{ThO}_4$ , and chlorine being both estimated. Two determinations gave  $\text{Th} = 223.2$  and 223.3, or about ten units below the accepted figures. In another sample the value 222.13 was found. To the unknown contamination, which raises the atomic weight of the metal and increases the density of the oxide, an atomic weight of from 260 to 280 must be attributed. This element Baskerville proposes to name carolinium. His paper is confessedly a preliminary communication, and further investigation is in progress. Since his methods of research differ from those of Brauner, the convergence of the results is all the more suggestive.

#### OLDER DATA.

In Bolton's "Index to Academic Dissertations," published by the Smithsonian Institution, I find the titles of four Russian theses which seem to have escaped the attention of all other writers on atomic weights. Of their value I can say nothing, but as they form part of the literature of the subject I reproduce the titles (as translated in Bolton's work) here.

*Dobrovolsky, V.* "Contributions to the Chemistry of Boron and Its Compounds. 1. The Atomic Weight of Boron." Kiev, 1869.

*Einbrodt, Paul.* "On the Atomic Weight of Nitrogen." Kharkov, 1840.

*Struve, H.* "Dissertation on the Determination of the Atomic Weight of Some Elements." St. Petersburg, 1850.

*Viluef, V.* "Dissertation on the Atomic Weight of Bismuth." St. Petersburg, 1849.

It is to be hoped that some scholar, having access to Russian literature, may prepare abstracts of these documents, and thereby make the data which are contained in them available for general use.

<sup>1</sup> This Journal, 23, 761

## THE STANDARD OF ATOMIC WEIGHTS.

Over this question, controversy still continues. The international committee of the German Chemical Society publishes its table for 1901 according to both standards; first with  $O = 16$ , and then in response to a demand from teachers giving a "didactic table" based upon  $H = 1$ . Both tables are given in this report, at the end. In their third general report<sup>1</sup> the same committee publish many letters from individual chemists, the final outcome from all sources being 106 voices in favor of  $H = 1$ , and 78 for  $O = 16$ . This preponderance is offset by the fact that five societies expressed their views as societies, four for  $O = 16$ , and only one for the hydrogen basis. The committee, therefore, continues to recommend the oxygen standard. The members of the Verein deutscher Chemiker who protested against the oxygen standard, also publish the results of their canvass among the teachers of chemistry in German-speaking countries<sup>2</sup>, and give the names of the respondents. 104 favored the hydrogen unit; 19 preferred the oxygen standard. Erdman<sup>3</sup> has printed a table of atomic weights with  $H = 1$ , which is in most points identical with that of your committee, only it is carried out uniformly to two decimal places. The two values in which it varies essentially from ours is in  $Co = 58.80$ , or about  $\frac{1}{4}$  unit higher, and in  $Pd = 106$  or  $\frac{1}{16}$  lower.

In favor of the oxygen standard there is a paper by Richards,<sup>4</sup> and the incidental remarks by Sakurai<sup>5</sup> in his essay upon "Some Points in Chemical Education." There is also, on the hydrogen side of the discussion, an elaborate article by Glücksmann.<sup>6</sup>

Still another standard of values has been proposed by Hinrichs,<sup>7</sup> who takes as the experimental basis of his system the atomic weight of "carbon-diamond" as 12 exactly. He seeks to show that all true atomic weights are multiples of the half-unit of hydrogen, but his method of discussion is more polemical than scientific. He reiterates his well-known objections to the work of

<sup>1</sup> *Ber. d. chem. Ges.*, 34, 4358.

<sup>2</sup> *Ztschr. angew. Chem.*, February 19, 1901.

<sup>3</sup> *Ibid.*, August 20, 1901.

<sup>4</sup> *Ztschr. anorg. Chem.*, 28, 355.

<sup>5</sup> Read before the Chemical Section of the British Association, 1901. Separately printed.

<sup>6</sup> *Ztschr. des. allgem. österr. Apotheker-Vereins*, Nos. 23, 24, 25, 26, 1901.

<sup>7</sup> "The Absolute Atomic Weights of the Chemical Elements, etc." Published at St. Louis, Mo., 1901.

Stas and the "Stasians," and denounces the conclusions of these men as "false and fraudulent."

#### MISCELLANEOUS NOTES.

Benoist,<sup>1</sup> studying the "specific opacity" of substances with regard to the X-rays, finds that for the elements this property is a definite function of the atomic weight. Applying this principle to certain compounds of indium he shows that the atomic weight of that element must be 113.4 rather than 75.6. That is, the classification of indium as trivalent and not as a dyad is confirmed.

Chabrié and Rengade<sup>2</sup> reach the same conclusion from an ebullioscopic determination of the molecular weight of indium acetylacetate.

In the report of this committee for 1900, Demarçay's work on the atomic weight of samarium was cited. He then found the oxide hitherto studied to have been contaminated with another earth of higher atomic weight. Continuing the investigation he has isolated this earth,<sup>3</sup> which corresponds to a new metal of atomic weight 151. To this metal he gives the name *Europium*.

G. and E. Urbain,<sup>4</sup> by a prolonged fractionation of the yttria groups, have obtained yttria and ytterbia in a high degree of purity. The atomic weights of the two metals are given, without details, as

$$\text{Yt} = 88.6.$$

$$\text{Yb} = 172.6.$$

These values are presumably based upon  $\text{O} = 16$ .

A new earth, resembling and associated with zirconia, has been separated by Hofmann and Prandtl<sup>5</sup> from euxenite. They assume that the metal is a tetrad, and determine its atomic weight from two analyses of separate fractions of the sulphate.

Weight of sulphate.	Weight of oxide.	Atomic weight.
0.2176	0.1234	177.6
0.1170	0.0664	177.9

These data are only preliminary, and further investigation is promised.

Strutt<sup>6</sup> has applied the calculus of probabilities to the tendency

<sup>1</sup> *Compt. rend.*, 132, 772. See also pages 324, 545.

<sup>2</sup> *Ibid.*, 132, 472.

<sup>3</sup> *Ibid.*, 132, 1484.

<sup>4</sup> *Ibid.*, 132, 136.

<sup>5</sup> *Ber. d. chem. Ges.*, 34, 1064.

<sup>6</sup> *Phil. Mag.*, (6), 1, 311.

exhibited by atomic weights to approximate whole numbers. No atomic weight can vary from a whole number by more than 0.5. Taking the eight elements Br, C, Cl, H, N, K, Na, and S, and assuming  $O = 16$ , the sum of the eight deviations from whole numbers is only 0.809. The probability that this sum should not be larger, is represented by about one chance in one thousand. Hence the atomic weights tend to approximate the whole numbers to a greater extent than can be accounted for by accident. As Strutt puts the case—"We have stronger reasons for believing in the truth of some modification of Prout's law than in that of many historical events which are universally accepted as unquestionable." A similar discussion, applied to eighteen elements, was once put forth by Mallet, but the mathematical treatment was not the same. There is also a short paper on the same subject by Rudolphi.<sup>1</sup>

## TABLE OF ATOMIC WEIGHTS.

The following table of atomic weights is somewhat differently arranged from that of a year ago. First your committee gives its own list, followed by that of the German Chemical Society on the basis of  $H = 1$ . Then come the three columns, Clarke, Richards,<sup>2</sup> and the German,<sup>3</sup> on the standard of  $O = 16$ .

In the light of the foregoing report, some of the values given in the table must be regarded as doubtful. Demarçay's work on samarium, Baskerville's and Brauner's on thorium, and Brauner's upon the other rare earth metals should be taken into account. All of this work, however, needs to be carried further and published more fully before the table should be correspondingly changed. The magnitude of the necessary changes is as yet too uncertain. In the case of thorium, the atomic weight given relates to that mixture of earths which has hitherto been called thoria, and which we actually meet in analytical operations.

	H = 1.		O = 16.		
	Clarke.	German.	Clarke.	Richards.	German.
Aluminum .....	26.9	26.9	27.1	27.1	27.1
Antimony. ....	119.5	119.1	120.4	120.0	120.
Argon .....	39.6	39.6	39.96	39.92	39.9
Arsenic .....	74.45	74.4	75.0	75.0	75.
Barium .....	136.4	136.4	137.40	137.43	137.4

<sup>1</sup> *Chem. Zeitung*, 28, 1133.

<sup>2</sup> *Proceedings American Academy*, April, 1901.

<sup>3</sup> Accompanying No. 1 of the *Berichte* for 1901, as an extra insertion.

	H = 1.		O = 16.		
	Clarke.	German.	Clarke.	Richards.	German.
Bismuth .....	206.5	206.9	208.1	208.	208.5
Boron .....	10.9	10.9	11.0	11.0	11.
Bromine .....	79.35	79.36	79.95	79.955	79.96
Cadmium .....	111.55	111.6	112.4	112.3	112.4
Caesium .....	131.9	132.	132.9	132.9	133.
Calcium .....	39.8	39.7	40.1	40.1	40.
Carbon .....	11.9	11.91	12.0	12.001	12.00
Cerium .....	138.0	139.	139.0	140.	140.
Chlorine .....	35.18	35.18	35.45	35.455	35.45
Chromium .....	51.7	51.7	52.1	52.14	52.1
Cobalt .....	58.55	58.56	59.00	59.00	59.
Columbium .....	93.0	93.3	93.7	94.	94.
Copper .....	63.1	63.1	63.60	63.60	63.6
Erbium .....	164.7	164.8	166.0	166.	166.
Fluorine .....	18.9	18.9	19.05	19.05	19.
Gadolinium .....	155.2	155.	156.4	156. ?	156.
Gallium .....	69.5	69.5	70.0	70.0	70.
Germanium .....	71.9	71.5	72.5	72.5	72.
Glucinum .....	9.0	9.03	9.1	9.1	9.1
Gold .....	195.7	195.7	197.2	197.3	197.2
Helium .....	3.93	4.0	3.96	3.96	4.
Hydrogen .....	1.000	1.00	1.008	1.0075	1.01
Indium .....	113.1	113.1	114.0	114.	114.
Iodine .....	125.89	125.90	126.85	126.85	126.85
Iridium .....	191.7	191.5	193.1	193.0	193.
Iron .....	55.5	55.6	55.9	55.9	56.
Krypton .....	81.15	81.2	81.76	81.7	81.8
Lanthanum .....	137.6	137.	138.6	138.5	138.
Lead .....	205.36	205.35	206.92	206.92	206.9
Lithium .....	6.97	6.98	7.03	7.03	7.03
Magnesium .....	24.1	24.18	24.3	24.36	24.36
Manganese .....	54.6	54.6	55.0	55.02	55.
Mercury .....	198.50	198.8	200.0	200.0	200.3
Molybdenum .....	95.3	95.3	96.0	96.0	96.
Neodymium .....	142.5	142.5	143.6	143.6	143.6
Neon .....	19.8	19.9	19.94	19.94	20.
Nickel .....	58.25	58.3	58.70	58.70	58.7
Nitrogen .....	13.93	13.93	14.04	14.04	14.04
Osmium .....	189.6	189.6	191.0	190.8	191.
Oxygen .....	15.88	15.88	16.000	16.000	16.00
Palladium .....	106.2	105.2	107.0	106.5	106.
Phosphorus .....	30.75	30.77	31.0	31.0	31.0
Platinum .....	193.4	193.3	194.9	195.2	194.8
Potassium .....	38.82	38.86	39.11	39.14	39.15
Praseodymium .....	139.4	139.4	140.5	140.5	140.5
Rhodium .....	102.2	102.2	103.0	103.0	103.0

	H = 1.		O = 16.		
	Clarke.	German.	Clarke.	Richards.	German.
Rubidium.....	84.75	84.76	85.4	85.44	85.4
Ruthenium .....	100.9	100.9	101.7	101.7	101.7
Samarium.....	149.2 ?	148.9	150.3 ?	150.	150.
Scandium .....	43.8	43.8	44.1	44.	44.1
Selenium .....	78.6	78.5	79.2	79.2	79.1
Silicon.....	28.2	28.2	28.4	28.4	28.4
Silver.....	107.11	107.12	107.92	107.93	107.93
Sodium .....	22.88	22.88	23.05	23.05	23.05
Strontium.....	86.95	86.94	87.60	87.68	87.6
Sulphur .....	31.83	31.83	32.07	32.065	32.06
Tantalum .....	181.5	181.6	182.8	183.	183.
Tellurium.....	126.1	126.	127.7	127.5 ?	127.
Terbium .....	158.8	....	160.	160.	....
Thallium.....	202.61	202.6	204.15	204.15	204.1
Thorium .....	230.8 ?	230.8	232.6 ?	233.	232.5
Thulium .....	169.4	170.	170.7	171. ?	171.
Tin .....	118.1	117.6	119.0	119.0	118.5
Titanium .....	47.8	47.7	48.15	48.17	48.1
Tungsten .....	182.6	182.6	184.	184.	184.
Uranium .....	237.8	237.7	239.6	238.5 <sup>1</sup>	239.5
Vanadium .....	51.0	50.8	51.4	51.4	51.2
Xenon .....	127.	127.	128.0	128.	128.
Ytterbium .....	171.9	172.	173.2	173.	173.
Yttrium.....	88.3	88.3	89.0	89.0	89.
Zinc.....	64.9	64.9	65.4	65.40	65.4
Zirconium .....	89.7	90.0	90.4	90.6	90.7

## METALLIC SOAPS FROM LINSEED OIL. AN INVESTIGATION OF THEIR SOLUBILITIES IN CERTAIN OF THE HYDROCARBONS.

BY HERMANN T. VULTÉ AND HARRIET WINFIELD GIBSON.

Received October 19, 1901.

IN the analysis of mixed paints, two of the most important points to be determined are the nature and the amount of the drying agent contained therein, since upon the quality of the drier present the value of the paint is largely conditioned. In modern practice, the driers used are almost invariably either the manganese or the lead soaps of linseed oil (so-called linoleates) or they are the resinates of the same metals, or they may be any mixture of these salts. The investigation of paint driers, therefore, resolves itself into a determination of the four salts mentioned. The method ordinarily pursued has been to separate the

<sup>1</sup> From unpublished determinations by Richards and Merigold.

base and the drier from the pigment by means of petroleum ether, the ethereal solution being then transferred to a tightly corked Erlenmeyer flask, and allowed to stand for from twelve to twenty-four hours. A somewhat gummy sediment, white to yellow in color and more or less adherent to the sides of the flask, is deposited. The sediment is then separated from the ethereal solution, and carefully washed by decantation with a further quantity of the petroleum ether. As, upon analysis, this sediment may be shown to consist mainly of the lead soap of linseed oil, together with some manganese soap, it has been assumed that a complete separation of the drier took place at this point and it was, therefore, believed that this method could be used in determining the character and amount of the drier. Upon further trial this method has proved far from satisfactory and various hydrocarbons, ranging from petroleum ether to benzine, have been suggested as a substitute for the solvent employed. None of these substitutes has been found to effect a perfect separation of the drier, although a distinct difference in solvent action has been observed. For example, the lead salts precipitate most quickly from petroleum ether and least from benzine, while the manganese salts are, in comparison, but slightly affected by either, except on long standing.

Since, then, a perfect separation of the drier from the base cannot be effected by any known solvent, it has been thought advisable to study the behavior of various metallic salts of linseed oil with different hydrocarbon solvents, and to determine the percentages of solubility at the end of stated and uniform periods. The work has been extended to cover the linseed oil soaps of most of the common metals, and the results of the investigation are given in the following paper.

The sodium soap of linseed oil was first prepared, great care being taken to effect complete saponification. The soap was curded out by excess lye, the use of salt being avoided. It was then washed free of impurities as far as possible, framed and allowed to stand until perfectly hard and dry. The soap thus formed was light brown in color, and had a pronounced odor of linseed. With water it formed a golden yellow solution and afforded an abundant lather.

A table follows, giving the petroleum solvents used, together with their boiling-points and specific gravities :



	Boiling-point.	Sp. gr. at 15° C.
Petroleum ether.....	35°-55°	0.639
Benzine.....	55°-75°	0.702
Benzine.....	75°-85°	0.695
Naphtha.....	59°	0.741
Naphtha.....	62°	0.732
Benzine.....	71°	0.698
Gasolene.....	74°	0.699
Turpentine .....	...	0.855

In the preparation of the various metallic soaps whose solubility it was desired to test, a water solution of the sodium soap was first carefully cooled to 20° C. or below. This is essential, as many of the metallic soaps examined have a very low melting-point. A soluble salt of the metal in question, exhibiting its lower valency if possible, was then selected, and a solution of this salt slowly added to the soap solution until precipitation ceased. The metallic soap was then washed by decantation with distilled air-free water, carefully dried, an excess amount added to each solvent, and the solutions allowed to stand in the dark. At the expiration of one hour, twenty-four hours, and forty-eight hours, 10 cc. of the clear solution were carefully evaporated in a tared watch-glass over a water-bath and the gain in weight recorded as dissolved matter. From this, the actual percentages of solubility were calculated and the results obtained, together with any peculiarities of the different salts, will be found in the annexed tables. It was thought well to first classify the metals into groups according to the ordinary method pursued for qualitative analysis, and then to give a résumé of the properties developed by each salt. For purposes of comparison, their solubility in turpentine, under the same conditions, is also given in these tables:

TABLES GIVING THE AMOUNT OF DISSOLVED MATTER IN THE  
VARIOUS SOLVENTS.

GROUP ONE.

*Lead.*

		35°-55°.	55°-75°.	75°-85°.	59°.	62°.	71°.	74°.	Turpa.
1 hr.	gms.	0.0385	0.0276	0.0477	0.0309	0.0276	0.0296	0.0405	0.2494
	p. ct.	0.602	0.393	0.686	0.417	0.377	0.424	0.579	2.917
24 hrs.	gms.	0.0381	0.0277	0.0479	0.0318	0.0278	0.0286	0.0413	0.2490
	p. ct.	0.598	0.394	0.689	0.428	0.379	0.409	0.591	2.912
48 hrs.	gms.	0.0376	0.0277	0.0471	0.0328	0.0273	0.0277	0.0420	0.2510
	p. ct.	0.590	0.394	0.678	0.443	0.373	0.398	0.601	2.935

## 218 HERMANN T. VULTÉ AND HARRIET WINFIELD GIBSON.

## GROUP TWO.

*Mercury.*

		35°-55°.	55°-75°.	75°-85°.	59°.	62°.	71°.	74°.	Turps.
1 hr.	gms.	0.0138	0.0057	0.0085	0.0041	0.0067	0.0027	0.0093	0.1692
	p. ct.	0.216	0.081	0.122	0.055	0.091	0.039	0.133	1.979
24 hrs.	gms.	0.0376	0.0475	0.0356	0.0155	0.0359	0.0147	0.0542	0.2544
	p. ct.	0.588	0.677	0.512	0.209	0.190	0.211	0.776	2.975
48 hrs.	gms.	0.0500	0.0782	0.0672	0.0552	0.0435	0.0384	0.0899	0.4593
	p. ct.	0.782	1.114	0.967	0.745	0.594	0.550	1.286	5.372

*Copper.*

		35°-55°.	55°-75°.	75°-85°.	59°.	62°.	71°.	74°.	Turps.
1 hr.	gms.	0.0285	0.0257	0.0145	0.0087	0.0124	0.1135	0.0609	0.1238
	p. ct.	0.449	0.336	0.209	0.117	0.169	1.626	0.871	1.448
24 hrs.	gms.	0.2516	0.3652	0.0962	0.1151	0.1094	0.1213	0.1032	0.4847
	p. ct.	3.962	5.202	1.384	1.553	1.494	1.738	1.476	5.669
48 hrs.	gms.	0.2534	0.4173	0.0977	0.1822	0.1172	0.1414	0.1886	0.6625
	p. ct.	3.992	5.944	1.406	2.459	1.601	2.026	2.698	7.748

## GROUP THREE.

*Tin.*

		35°-55°.	55°-75°.	75°-85°.	59°.	62°.	71°.	74°.	Turps.
1 hr.	gms.	0.0435	0.0776	0.0926	0.0600	0.0804	0.0928	0.1216	0.2401
	p. ct.	0.681	1.105	1.332	0.809	1.098	1.329	1.739	2.808
24 hrs.	gms.	0.0520	0.0780	0.0921	0.0626	0.0867	0.0935	0.1322	0.2408
	p. ct.	0.801	1.111	1.325	0.844	1.184	1.339	1.891	2.816
48 hrs.	gms.	0.0601	0.0787	0.0922	0.0661	0.0885	0.0933	0.1389	0.2352
	p. ct.	0.940	1.121	1.326	0.892	1.209	1.336	1.987	2.751

*Antimony.*

		35°-55°.	55°-75°.	75°-85°.	59°.	62°.	71°.	74°.	Turps.
1 hr.	gms.	0.0766	0.0877	0.0897	0.0703	0.1069	0.0785	0.0608	0.3496
	p. ct.	1.198	1.249	1.291	0.948	1.462	1.124	0.869	4.088
24 hrs.	gms.	0.1051	0.0965	0.0974	0.0702	0.1088	0.0814	0.0698	0.3446
	p. ct.	1.631	1.374	1.401	0.947	1.486	1.166	0.998	4.023
48 hrs.	gms.	0.1306	0.1155	0.1041	0.0742	0.1104	0.0903	0.0746	0.3432
	p. ct.	2.043	1.645	1.498	1.001	1.508	1.294	1.067	4.014

## GROUP FOUR.

*Iron.*

		35°-55°.	55°-75°.	75°-85°.	59°.	62°.	71°.	74°.	Turps.
1 hr.	gms.	0.1887	0.2570	0.2589	0.2878	0.2635	0.2087	0.1873	0.6103
	p. ct.	2.953	3.661	3.725	3.884	3.599	2.989	2.679	7.138
24 hrs.	gms.	0.3105	0.2985	0.3139	0.3287	0.2840	0.1999	0.1897	0.6424
	p. ct.	4.859	4.252	4.516	4.436	3.878	2.864	2.711	7.513
48 hrs.	gms.	0.2484	0.2251	0.2483	0.2895	0.2130	0.1535	0.1511	0.6424
	p. ct.	3.887	3.206	3.572	3.907	2.909	2.199	2.161	7.513

*Chromium.*

	35°-55°.	55°-75°.	75°-85°.	59°.	62°.	71°.	74°.	Turpa.
1 hr.	gms. 0.0455	0.0539	0.0645	0.0620	0.0579	0.0595	0.0592	0.2293
	p. ct. 0.712	0.768	0.928	0.837	0.791	0.852	0.847	2.682
24 hrs.	gms. 0.0473	0.0646	0.0598	0.0902	0.0729	0.0579	0.0597	0.3822
	p. ct. 0.740	0.920	0.860	1.217	0.992	0.829	0.854	4.470
48 hrs.	gms. 0.0520	0.0459	0.0501	0.0571	0.0551	0.0497	0.0485	0.3853
	p. ct. 0.814	0.654	0.721	0.772	0.753	0.712	0.694	4.506

*Aluminum.*

	35°-55°.	55°-75°.	75°-85°.	59°.	62°.	71°.	74°.	Turpa.
1 hr.	gms. 0.0045	0.0033	0.0025	0.0022	0.0097	0.0067	0.0036	0.1796
	p. ct. 0.070	0.047	0.036	0.029	0.132	0.096	0.052	2.101
24 hrs.	gms. 0.0422	0.0610	0.0439	0.0199	0.0378	0.0514	0.0351	0.1898
	p. ct. 0.660	0.868	0.632	0.268	0.516	0.736	0.502	2.219
48 hrs.	gms. 0.0940	0.1038	0.0763	0.0457	0.0570	0.0718	0.0509	0.1941
	p. ct. 1.471	1.479	1.097	0.617	0.779	1.029	0.728	2.270

## GROUP FIVE.

*Nickel.*

	35°-55°.	55°-75°.	75°-85°.	59°.	62°.	71°.	74°.	Turpa.
1 hr.	gms. 0.1094	0.1255	0.1282	0.0785	0.0851	0.1048	0.1127	0.2306
	p. ct. 1.709	1.788	1.845	1.059	1.162	1.501	1.612	2.697
24 hrs.	gms. 0.1933	0.1751	0.1874	0.1584	0.1046	0.1277	0.1487	0.3769
	p. ct. 3.025	2.494	2.696	2.138	1.429	1.829	2.127	4.408
48 hrs.	gms. 0.1856	0.1703	0.1807	0.1583	0.0559	0.0632	0.0873	0.3345
	p. ct. 2.904	2.425	2.600	2.136	0.763	0.905	1.249	3.912

*Cobalt.*

	35°-55°.	55°-75°.	75°-85°.	59°.	62°.	71°.	74°.	Turpa.
1 hr.	gms. 0.0172	0.0185	0.0201	0.0143	0.0176	0.0140	0.0082	0.3742
	p. ct. 0.269	0.263	0.289	0.193	0.243	0.200	0.116	4.376
24 hrs.	gms. 0.0204	0.0195	0.0209	0.0265	0.0270	0.0250	0.0157	0.2997
	p. ct. 0.319	0.278	0.301	0.358	0.369	0.358	0.225	3.505
48 hrs.	gms. 0.0262	0.0181	0.0210	0.0343	0.0386	0.0390	0.0271	0.3611
	p. ct. 0.410	0.257	0.302	0.463	0.527	0.558	0.388	4.223

*Manganese.*

	35°-55°.	55°-75°.	75°-85°.	59°.	62°.	71°.	74°.	Turpa.
1 hr.	gms. 0.2280	0.0998	0.0896	0.0721	0.0702	0.0673	0.1077	0.1827
	p. ct. 3.568	1.421	1.289	0.973	0.959	0.964	1.541	2.137
24 hrs.	gms. 0.2425	0.0990	0.0840	0.0899	0.0816	0.0854	0.0945	0.2098
	p. ct. 3.795	1.410	1.208	1.213	1.115	1.223	1.352	2.454
48 hrs.	gms. 0.0480	0.0276	0.0461	0.0282	0.0281	0.0288	0.0403	0.2749
	p. ct. 0.751	0.393	0.663	0.381	0.384	0.414	0.576	3.215

*Zinc.*

		35°-55°.	55°-75°.	75°-85°.	59°.	62°.	71°.	74°.	Turps.
1 hr.	gms.	0.0254	0.0492	0.0420	0.0310	0.0187	0.0424	0.0360	0.1870
	p. ct.	0.397	0.701	0.604	0.418	0.255	0.607	0.515	2.187
24 hrs.	gms.	0.0536	0.0792	0.0865	0.0674	0.0640	0.0719	0.0706	0.2530
	p. ct.	0.838	1.128	1.245	0.909	0.874	1.031	1.010	2.959
48 hrs.	gms.	0.0606	0.0715	0.0903	0.0649	0.0663	0.0846	0.0853	0.2946
	p. ct.	0.948	1.018	1.299	0.876	0.905	1.212	1.220	3.445

## GROUP SIX.

*Barium.*<sup>1</sup>

		35°-55°.	55°-75°.	75°-85°.	59°.	62°.	71°.	74°.	Turps.
1 hr.	gms.	0.0066	0.0022	0.0015	0.0031	0.0072	0.0017	0.0007	0.1228
	p. ct.	0.103	0.031	0.021	0.042	0.098	0.024	0.001	1.436
24 hrs.	gms.	0.0062	0.0040	0.0013	0.0024	0.0143	0.0031	0.0027	0.1301
	p. ct.	0.097	0.057	0.019	0.032	0.195	0.044	0.039	1.522

*Calcium.*<sup>1</sup>

		35°-55°.	55°-75°.	75°-85°.	59°.	62°.	71°.	74°.	Turps.
1 hr.	gms.	0.0154	0.0051	0.0053	0.0011	0.0109	0.0133	0.0045	0.1022
	p. ct.	0.241	0.072	0.076	0.015	0.149	0.191	0.064	1.195
24 hrs.	gms.	0.0120	0.0064	0.0049	0.0009	0.0098	0.0127	0.0042	0.1274
	p. ct.	0.188	0.091	0.070	0.012	0.134	0.182	0.064	1.490

## CONCLUSION.

A comparison of the figures given in the foregoing tables discloses the fact that certain of these metallic soaps, namely, those made of lead, nickel, iron and manganese, show marked individuality, the characteristics of each not being repeated by any other soap.

1. The lead soap goes almost completely out of solution from all the petroleum solvents in less than one hour.

2. The nickel soap, while eventually affording a nearly complete separation, remains in solution for several days.

3. The iron soap, while giving a permanent solution of steadily increasing weight (due to oxidation), is an excellent drier on the application of slight heat.

4. The manganese soap is unique in its drying properties.

As thus far conducted, the foregoing investigation discloses the following facts:

1. The percentage of separation of the metallic soaps of linseed oil from their solutions in the hydrocarbon solvents is vari-

<sup>1</sup> The percentage of dissolved matter was so small in the cases of barium and calcium that the investigation was dropped at the expiration of twenty-four hours.

## RESUMÉ OF ACTION OF PETROLEUM SOLVENTS ON METALLIC SOAPS OF LINSEED OIL.

	Character of soap.	Residue from evaporation.	Boiling-point of most active solvent.	Permanence of solution.
I Lead .....	White; granular; oxidizes to yellow.	Colorless; hard lacquer.	35°-55°.	Nearly complete separation in 1 hour.
II Mercury .....	White; curdy.	Soft; colorless.	74°.	Gain in weight all solvents.
Copper .....	Pale green; curdy; oxidizes to deep green.	Bright green lacquer; rather soft.	55°-75°.	Gain in weight all solvents; nearly constant after 24 hours.
III Tin .....	Yellow-white; scanty; granular to slimy.	Oily smear.	74°.	Nearly constant weight.
Antimony ...	Yellow-white; plentiful; soft; granular.	Oily smear.	62°.	Nearly constant weight.
IV Iron .....	Gray-green; oxidizes to red-brown very quickly.	Mahogany lacquer; rather soft.	35°-55°.	Maximum at 24 hours; loss slight.
Chromium ..	Purplish gray; oxidizes to purplish green.	Bright green lacquer; quite hard.	59°.	Slight loss after 24 hours.
Aluminum ..	White; granular; oxidizes to yellow.	Hard colorless lacquer.	55°-75°.	Gain in weight all solvents.
V Nickel .....	Apple-green; granular.	Pale green lacquer.	35°-55°.	Permanent several days; then nearly complete separation.
Cobalt .....	Purplish red; granular.	Soft; reddish.	62° (sol'n slight.)	Sol'n and sep'n slight.
Manganese ..	Brownish; curdy; rapidly oxidizes to dark brown.	Brown lacquer; hard.	35°-55°.	Maximum at 24 hours; partial sep'n at 48 hours.
Zinc .....	White; curdy.	Oily smear.	75°-85°.	Uniform after 24 hours.
VI Barium .....	White; curdy.	Oily smear.		
Calcium .....	White; curdy.	Oily smear.		

Very slight solubility.  
Very slight solubility.

able, differing with the nature of the solvent and the character of the linoleate.

2. Each metallic soap affords a maximum percentage of solubility in some special hydrocarbon and, therefore, no one hydrocarbon solvent can be commended for all metals.

3. The time at which the maximum separation takes place is also variable, differing with the metal employed.

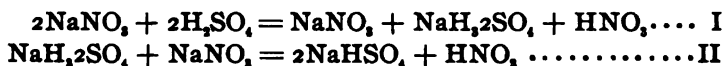
It is, therefore, evident that a knowledge of the behavior of each soap with the different solvents is essential to the general analysis of driers and it is with the hope of contributing to this knowledge that the present paper is submitted.

### ON THE DECOMPOSITION OF SODIUM NITRATE BY SULPHURIC ACID. PART III.

By C. W. VOLNEY.

Received November 12, 1901.

FROM results of previously reported work, the author concluded<sup>1</sup> that the action of sulphuric acid on sodium nitrate takes place in two distinct phases, expressed by :



and that these two phases of the process are marked by distinctly different temperatures.

To obtain direct evidence for these conclusions, I have extended the experimental part of the investigation by producing in the retorts for distillation the exact condition for each phase, by using the materials, as represented therein.

For the first phase, 85 grams of dry sodium nitrate with 200 grams of concentrated sulphuric acid were subjected to distillation, according to I. The distillation was carried out in the manner and apparatus already described, which gave observations for the temperatures of applied heat, the retort contents and distilling acid.

In the following are given the results of this distillation, as they were observed :

<sup>1</sup> This Journal, 23, 490.

Time. A.M.	Outside. °C.	Retort content. °C.	Distilled acid. °C.	Remarks.
8	23	23	23	{ No rise in temperature; heat applied at 8:30; contents of retort dissolve to a clear liquid.
9	90	25	..	
10	90	25	..	
10:12	118	74	..	
10:15	123	81	50	Gas bubbles show in liquid.
10:25	125.5	98	63	{ The liquid commences to boil; gases condense.
10:35	122	104	70	
10:40	135	105	83	Foaming; distillation commences.
10:47	144	107	86	Distils well; foaming; lessen fire.
11:25	125	107	85	
	113	109	85	
	112	107	60	Increase fire.
11:30	147	109	82	Distils well.
	135	106	83	{ Liquid in retort boiling quietly; distils well.
12:15	142	127	72	
12:50	162	130	82	{ Sulphates separate in liquid in retort; salts collect on surface.
P.M.				
1	171	128	81	
1:30	176	128	81.5	Distils well.
2	180	130	81.5	
3	178	132	81.5	Liquid quiet.
3:40	180	136	80	No more gas escaping.
4	180	131	72	Distillation ceases.

The acid collected was of 1.517 sp. gr. at 18°–19°; it was almost colorless and weighed 64.2 grams.

The residue in the retort solidified, on cooling, to elongated prismatic crystals with rhombic base. It weighed 219 grams.

The loss in the observation amounted therefore to 2.8 grams, and is evidently caused by escape of nitrous gases.

An observation of the temperatures shows that the acid distils under these conditions, *i. e.*, when 2 molecules of sulphuric acid to 1 of nitrate are used, in the following manner:

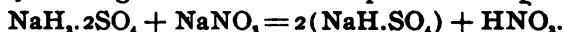
The minimum of applied heat was 123°, the maximum 180°; 160° may be considered an average; the temperatures of the salt in the retort are expressed by 81° and 140°, and may be given as 100° in average, and the temperatures of the distilling acid vapors vary between 80° and 90°, so that the boiling-point of the nitric acid produced is about 81.5°.

Under the conditions given, that is, by using two molecules of sulphuric acid to one molecule of nitrate, the decomposition of the latter can, therefore, be effected at about  $100^{\circ}$  and the acid distilled at  $82^{\circ}$ .

The residue in the retorts corresponds with the trisulphate described before. It shows the same crystallization and composition. But it can also be prepared by adding to dry sodium disulphate two molecules of concentrated sulphuric acid and melting it at  $80^{\circ}$ – $90^{\circ}$ , whereby, a clear liquid is obtained which, on cooling, furnishes the crystals. The same crystals are produced when dry sodium disulphate or monosulphate is dissolved in an excess of concentrated sulphuric acid at a temperature of  $90^{\circ}$ , when, on cooling, the formed trisulphate crystallizes from the liquid and may be obtained free from adhering sulphuric acid by filtration *in vacuo* or a current of dry air. On a platinum filter they can be repeatedly washed with sulphuric acid without losing their crystalline shape or luster, as long as access of moisture is prevented; these observations may be readily performed in the apparatus already described.<sup>1</sup>

To preserve this salt, perfectly dry bottles must be used and the air excluded. This trisulphate gives 60.51 per cent. of normal sodium sulphate, and the salts from the residues in the retorts above described, gave an average from determinations of 58 per cent., which compares with the theoretical percentage of 60.56 sufficiently to agree with the theory of decomposition assumed by me.

I have prepared larger quantities of this polysulphate to be used in my investigation of the second phase of the process:



Accordingly, 218 grams of the trisulphate and 85 grams of sodium nitrate were treated in the retort in the manner already described, and the following table shows the results of distillation. When the two dry salts are brought in contact, no reaction takes place and no change of temperature is observed.

On heating, no decomposition can be noticed until the thermometer in the retort indicates  $155^{\circ}$ , when some yellow vapors make their appearance.

A distinct reaction is perceptible when the contents of the retort show  $167^{\circ}$ .

<sup>1</sup> This Journal, 23, 490.

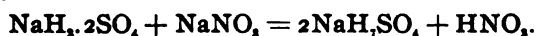


Time. A.M.	Outside. °C.	Retort content. °C.	Distilled acid. °C.	Remarks.
11	22	22	..	No reaction.
12	22	22	..	No reaction.
12:30	..	..	..	Heat applied to retort.
P.M.				
1	155	96	40	Slight yellow vapors.
1:35	167	110	60	Reaction shows boiling.
	178	112	..	Red vapors.
	185	118	70	{ Contents of retort liquid, red vapors condensing.
	200	120	80	Commences to distil.
2	210	121	85	Yellow acid distilling.
	225	122	85	Yellow acid distilling.
	230	127	90	Yellow acid distilling.
2:30	240	125	95	Yellow acid distilling.
	260	127	98	Yellow acid distilling.
	265	140	109	Distilling rapidly.
3	270	160	122	Distilling rapidly.
3:30	270	167	120	Distilling rapidly.
4	270	167	120	Distilling rapidly.
4:10	280	168	119	Distillation lessens.
4:30	280	168	107	Distillation lessens.
5	280	167	69	Distillation ceases.
6	278	168	60	Stop heating.

The acid, resulting from this process, was yellow to red, showed a specific gravity of 1.526 at 21.10°, and weighed 52 grams. The residue in the retort solidified, on cooling, to a white crystalline mass and weighed 242.5 grams.

By calcining 1.3 grams of this salt, 0.74 gram sodium sulphate was obtained; loss, 0.56 gram. Considering this residual salt as NaHSO<sub>4</sub> (the disulphate), theory would require the neutral salt to be 0.77 gram, and the loss as sulphuric acid to weigh 0.53 gram.

It is safe to assume that at the temperature under which the distillation took place, the residue is NaHSO<sub>4</sub>, and that the reaction of sodium trisulphate on sodium nitrate is correctly expressed by



The loss of 0.56 gram, representing 6 per cent., is caused by decomposed acid and is probably greater in acid, than it does appear, as the weight of the residue is, by 2.5 grams, greater than it should be. The observed temperatures show that the decomposition during the second phase of the process takes place under the application of outside heat indicated by 167°–280°;

that the acid distils at  $104^{\circ}$ – $122^{\circ}$  from the contents of the retort having a temperature of  $165^{\circ}$ ; and that the nitric acid, which is received during this phase, has been partly decomposed and forms the yellow- or red-colored acid.

The conclusions drawn from the foregoing experimental work, may be expressed as follows:

(1) At the common temperature, or below  $20$ , neither concentrated sulphuric acid nor the polysulphate act on sodium nitrate; the reaction is, at least, so very slow, that during a contact of three to four days, only traces of free nitric acid can be observed.

(2) At a higher temperature the nitrate is decomposed by sulphuric acid and the reaction is finished at temperatures below  $100^{\circ}$ , free nitric acid and  $\text{NaH}_2\text{SO}_4$  resulting.

(3) The trisulphate acts on the nitrate at temperatures over  $165^{\circ}$ , products of the reaction being again free nitric acid and sodium bisulphate.

(4) The nitric acid, resulting during this phase at the corresponding high temperature, is always decomposed; its vapors, in distilling over, show a temperature of about  $120^{\circ}$ – $123^{\circ}$ , and this acid was formerly considered the second hydrate of nitric acid,  $(\text{H}_2\text{O})_2\text{N}_2\text{O}_5$  (the  $(\text{HO})_2\text{NO}_3$  of old).

Under the conditions of the described experimental work, the water can be the result of decomposition only of nitric acid, and I have also shown that this can take place only during the second phase of the process.

NEW YORK, September 29, 1901.

[CONTRIBUTION FROM THE HAVEMEYER LABORATORIES, COLUMBIA UNIVERSITY. No. 60.]

### ON THE FERROCYANIDES OF CADMIUM.

BY EDMUND H. MILLER.

Received November 7, 1901.

IT has already been shown<sup>1</sup> that the results obtained in titrating cadmium by potassium ferrocyanide in a neutral or slightly acid solution do not agree with any of the formulas given for the precipitate, while the values obtained in an ammoniacal solution agree very closely with the formula  $\text{K}_2\text{CdFe}(\text{CN})_6$ .

The present work was undertaken to study the variation in composition under different conditions and, if possible, to assign

<sup>1</sup> Miller and Fisher: This Journal, Sept., 1900.

definite formulas to the precipitates so formed. To cover the ground as completely as possible, the following series of precipitates was made :

- A.* Neutral solution, cadmium in excess.
- B.* Neutral solution, ferrocyanide in excess.
- C.* Acid with hydrochloric, 10 cc. (sp. gr. 1.20) per liter, cadmium in excess.
- D.* Acid with hydrochloric, 10 cc. (sp. gr. 1.20) per liter, ferrocyanide in excess.
- E.* Acid with acetic, 10 cc. 50 per cent. acetic acid per liter, cadmium in excess.
- F.* Acid with acetic, 10 cc. 50 per cent. acetic acid per liter, ferrocyanide in excess.
- G.* Alkaline with ammonia,<sup>1</sup> cadmium in excess.
- H.* Alkaline with ammonia,<sup>1</sup> ferrocyanide in excess.

The precipitates were all formed in large beakers, in the cold and allowed to stand, then washed with water, water containing hydrochloric acid, water containing acetic acid, water and ammonia, respectively, so that the conditions of precipitation were maintained, then washed with water till free from excess of cadmium or of ferrocyanide. The work was begun in June, 1900, and the precipitates analyzed a year later.

In general, whenever the cadmium was in excess the precipitates settled well, and when ferrocyanide was in excess, very badly. The salts used for this series of precipitations were cadmium nitrate and potassium ferrocyanide.

The method of analysis was in all cases the same, and the object was to obtain the ratio between iron and potassium and cadmium. Some attempts were made at first to dry the precipitates to constant weight, but as decomposition resulted no attempt was made to weigh the portions taken for analysis but all the determinations were expressed as ratios.

The precipitates were repeatedly evaporated in casseroles with nitric and sulphuric acids till decomposition was complete, the residue was dissolved in water, the excess of sulphuric acid neutralized with ammonia and the cadmium precipitated as sulphide in a very weak hydrochloric acid solution, dissolved and de-

<sup>1</sup> The cadmium hydroxide was dissolved in an excess of ammonia before the potassium ferrocyanide was added.

terminated as phosphate.<sup>1</sup> In the filtrate the iron was, after oxidation, precipitated as hydroxide and weighed as ferric oxide. The filtrate from the iron was evaporated, the ammonium salts expelled and the potassium weighed as sulphate. In the determination of cadmium as phosphate, weighing as pyrophosphate, and as cadmium ammonium phosphate ( $\text{CdNH}_4\text{PO}_4 \cdot \text{H}_2\text{O}$ ) were tried and the weighing as cadmium ammonium phosphate adopted as more convenient.

The following is a brief description of the precipitates formed and the results obtained from their analysis expressed as an atomic ratio:<sup>2</sup>

*A* (neutral solution, cadmium in excess). Yellowish white, settled well, was washed (nine times) till free from cadmium; when dry, was yellowish-white, apparently slightly oxidized to ferricyanide. Gave, on analysis,  $\text{Fe}:\text{K}:\text{Cd}::1:1.14:1.42$  or  $7:8:10$ , corresponding to  $\text{K}_2\text{Cd}_{10}(\text{Fe}(\text{CN})_6)_7$ .

*B* (neutral, ferrocyanide in excess). White, settled partially after five months, was washed at intervals for a year. It was the most tedious of all but did not give evidence of decomposition. The ratio was  $\text{Fe}:\text{K}:\text{Cd}::1:1.80:1.08$ .

*C* (hydrochloric, cadmium in excess). Dull orange-yellow, settled very well; on washing with water containing 10 cc. concentrated hydrochloric acid per liter, the supernatant liquid became greenish with evident decomposition of the precipitate. A second lot was made under the same conditions; the precipitate, at first white, became yellow within a few seconds. The yellow precipitate is also formed when cadmium is dissolved in hydrochloric and a little nitric acid, then neutralized, 2 cc. of hydrochloric acid added, and then titrated by potassium ferrocyanide. It is not due to the presence of any nitroprusside and is undoubtedly due to the oxidation of part of the cadmium ferrocyanide to ferricyanide, which is brownish yellow, by the nitrate present in both cases. This precipitate was not analyzed.

*D* (hydrochloric, ferrocyanide in excess). The precipitate, at first yellowish, became white when an excess of potassium ferrocyanide was present; it settled quite well at first but badly after washing, like the others when an excess of ferrocyanide is

<sup>1</sup> Miller and Page: *School of Mines Quarterly*, July, 1901, and *Ztschr. anorg. Chem.*, 28, 233 (1901).

<sup>2</sup> These values are obtained by dividing the calculated weights of iron, potassium, and cadmium, by their atomic weights and then multiplying by  $\frac{1}{\text{wt. iron}}$ .

present, and showed a greenish-yellow color after washing, evidently due to a slight decomposition. The results were  $\text{Fe} : \text{K} : \text{Cd} :: 1 : 1.933 : 0.991$ , corresponding to  $\text{K}_2\text{CdFe}(\text{CN})_6$ .

*E* (acetic, cadmium in excess). The precipitate was nearly white, settled well, and on drying was white. The ratio was  $\text{Fe} : \text{K} : \text{Cd} :: 1 : 1.21 : 1.392$ , corresponding quite closely to  $\text{K}_4\text{Cd}_2(\text{Fe}(\text{CN})_6)_3$ .

*F* (acetic, cadmium in excess). Creamy white precipitate which settled badly and on drying was slightly greenish on the surface. The iron cadmium ratio was  $1 : 0.95$ , corresponding approximately to  $\text{K}_2\text{CdFe}(\text{CN})_6$ .

*G* (ammonia, cadmium in excess). A pure white precipitate which gave considerable trouble in testing for an excess of cadmium, as owing to the excess of cadmium dissolved in ammonia, a point was reached where either  $\text{FeCN}_6'''$  or  $\text{Cd}''$  ions gave a precipitate. The precipitate on washing became flocculent and settled immediately; it was washed six times with water containing ammonia and then with water until no test for cadmium was obtained. The analytical results gave the ratio  $\text{Fe} : \text{K} : \text{Cd} :: 1 : 0 : 3.33$ , a result impossible for a ferrocyanide. After rewashing with strong ammonia to dissolve out the excess of cadmium, which was undoubtedly present as either hydroxide or carbonate and which gave the flocculent character to the precipitate, the ratio became  $\text{Fe} : \text{Cd} :: 1 : 1.94$ , agreeing approximately with the normal ferrocyanide  $\text{Cd}_2\text{Fe}(\text{CN})_6$ .

*H* (ammonia, ferrocyanide in excess). Pure white precipitate which settles well at first, but poorly after washing.<sup>1</sup> In this case only, the iron cadmium ratio was determined; the figures obtained were  $1 : 0.97$ , corresponding to  $\text{K}_2\text{CdFe}(\text{CN})_6$ .

On account of the oxidation and decomposition of some of the precipitates just described, a second set of eight was made under exactly the same conditions, using cadmium chloride instead of nitrate. These were made in December, 1900, and are marked *A'*, *B'*, etc., so as to be readily compared with the preceding series.

*A'* (neutral, cadmium in excess). White precipitate, which settled well and was completely washed in a month. On analysis, the ratio found was  $\text{Fe} : \text{K} : \text{Cd} :: 1 : 1.14 : 1.448$  or  $7 : 8 : 10$ , agreeing with the results obtained in *A* and the formula  $\text{K}_5\text{Cd}_{10}(\text{Fe}(\text{CN})_6)_7$ .

<sup>1</sup> Washed six times with ammonia and water, then with water till free from ferrocyanide.

*B'* (neutral, ferrocyanide in excess). A slightly yellowish precipitate which did not settle at all; various methods were tried to hasten the settling, but without effect, so it was finally abandoned.

*C'* (hydrochloric, cadmium in excess). White precipitate which settled well, gave iron to cadmium 1:1.46 and 1:1.44. Results very similar to those obtained from *A* and agreeing with a ratio of Fe:K:Cd of 7:8:10.

*D'* (hydrochloric, ferrocyanide in excess). A greenish precipitate which would not settle. Separation by a centrifugal was tried as well as other methods such as the addition of sodium chloride but without effect, finally it became so decomposed as to be worthless.

*E'* (acetic, cadmium in excess). White, settled well, leaving a turbid solution; gave on analysis Fe:K:Cd :: 1:1.078:1.383.

*F'* (acetic, ferrocyanide in excess). This precipitate became very green on standing and was rejected.

*G* (ammonia, cadmium in excess). A perfectly white curdy precipitate which settles immediately, leaving a clear colorless liquid and differs entirely in physical properties from the preceding. It gave on analysis the ratio 1:0:2.27, showing, as in *G*, no potassium, and the presence of cadmium in excess of the possible ratio for a ferrocyanide.

*H'* (ammonia, ferrocyanide in excess). A creamy white precipitate which settles well and has the consistency of clay, requiring considerable force to stir it up, and differing entirely in physical properties from the others. It gave, on analysis, Fe:K:Cd :: 1:2.07:1.048 or nearly 1:2:1, corresponding to  $K_2CdFe(CN)_6$ .

It remained to obtain precipitates to take the places of *B'*, *D'*, and *F'*. So in March, 1901, these precipitates were made again under the conditions already described, but in dark brown glass bottles and were kept in the dark. This greatly lessened the decomposition and by sacrificing a large proportion of the precipitates with the wash-water by July, residues were obtained which were free from excess of ferrocyanide and only slightly bluish in color.

*B''* (neutral, ferrocyanide in excess). Ratio, 1:1.81:1.12, agreeing fairly with *B* and with  $K_{18}Cd_{11}(Fe(CN)_6)_{10}$ .

*D'* (hydrochloric, ferrocyanide in excess). Ratio, 1 : 2.02 : 0.955, confirming *D* and corresponding to  $K_2CdFe(CN)_6$ .

*F'* (acetic, ferrocyanide in excess). Ratio, 1 : 2.03 : 0.95, confirming *F* and corresponding to  $K_2CdFe(CN)_6$ .

The abnormal results in *G* and *G'*, probably due to cadmium hydroxide being carried down in varying quantities, necessitated a repetition of this work, so in July, 1901, *G'''* was made under the same conditions but was treated repeatedly with very large quantities of ammonia before washing with water and then analyzed at once.

*G'''* (ammonia, cadmium in excess). The iron cadmium ratio was determined in duplicate and found to be 1 : 1.496, corresponding to  $K_2Cd_3(Fe(CN)_6)_4$ .

When this precipitate was being washed it was noticed that there was a portion which did not settle as well as the rest; this was decanted from the part which settled well, washed and analyzed, giving a ratio of exactly 1Fe : 1Cd.

In the results already given the duplicates on *C'* and the ratios on *E* and *E'* did not check satisfactorily, so these precipitates were made again (July, 1901) and as they settled well (cadmium being in excess) they were washed and analyzed within a week.

*C'''* (hydrochloric, cadmium in excess). White, no decomposition; gave Fe : Cd : : 1 : 1.07 and 1 : 1.065.

*E'''* (acetic, cadmium in excess). White, no decomposition; gave Fe : Cd : : 1 : 1.07 and 1 : 1.06.

We see in these two a total lack of agreement in composition with those which were allowed to stand many months before analysis, indicating a change in composition after precipitation. On the other hand these last results are in exact agreement with the titration ratios in slightly acid solution;<sup>1</sup> for if the theory for  $1K_2Fe(CN)_6$  or 1Fe : 1Cd<sup>2</sup> gives for the strength of the ferrocyanide solution 1 cc. = 0.00671 gram cadmium, then, if the ratio in the precipitate is 1 : 1.07, the strength of the solution in terms of cadmium becomes  $1.07 \times 0.00671$  or 0.00718, while the average result of titration was 0.00717.

For ease of comparison let us disregard for the present the potassium, which has been found to be present always in the proper amount to satisfy the remaining valency of the ferrocyanogen radical and consider only the iron cadmium ratios.

<sup>1</sup> Miller and Fisher : This Journal, 21, 542 (1900).

<sup>2</sup> Based on Hermann's formula  $K_2CdFe(CN)_6$ .

Character of solution.	Cadmium in excess.	Ferrocyanide in excess.
	Fe : Cd.	Fe : Cd.
Neutral .....	1 : 1.42 A	1 : 1.08 B
	1 : 1.448 A'	1 : 1.12 B'
Hydrochloric .....	1 : 1.462 C'	1 : 0.99 D
	1 : 1.44 C'	1 : 0.955 D''
	1 : 1.07 C''' <sup>1</sup>	....
	1 : 1.065 C''' <sup>1</sup>	....
Acetic.....	1 : 1.392 E	1 : 0.95 F
	1 : 1.383 E'	1 : 0.95 F''
	1 : 1.07 E''' <sup>1</sup>	....
	1 : 1.06 E''' <sup>1</sup>	....
Ammonia .....	1 : 3.33 G	1 : 0.97 H
	1 : 1.94 G <sup>2</sup>	1 : 1.048 H'
	1 : 2.27 G'	....
	1 : 1.496 G'''	....
	1 : 1.496 G'''	....
	1 : 1 G''' <sup>3</sup>	

We see from the work described that :

(1) The results when ferrocyanide is in excess are entirely different from those where cadmium is in excess.

(2) In either acid or ammoniacal solution, ferrocyanide being in excess, the ratio is 1 iron to 1 cadmium or the precipitate is  $K_2CdFe(CN)_6$ , while in a neutral solution the cadmium ratio is higher.

(3) With cadmium in excess, in either neutral or hydrochloric acid solution the final composition is the same, corresponding to  $K_2Cd_{10}(Fe(CN)_6)_7$ , while in an acetic acid solution the final composition corresponds to  $K_2Cd_4(Fe(CN)_6)_3$ .

(4) With cadmium in excess, in an acid solution the composition alters on standing with an increase of cadmium in the ratio, but when freshly precipitated the ratio agrees exactly with the results by titration.

(5) With cadmium in excess, in an ammoniacal solution the ratio exceeds the normal, but after washing with ammonia corresponds to  $Cd_4Fe(CN)_6$ ; when freshly precipitated and washed quickly with ammonia, the part which settles badly being removed by decantation, the composition agrees exactly with  $K_2Cd_4(Fe(CN)_6)_3$ , while the part decanted corresponds to  $K_2CdFe(CN)_6$ .

<sup>1</sup> Analyzed within a week of precipitation.

<sup>2</sup> After treatment with ammonia.

<sup>3</sup> Decanted portion.



(6) The constancy of the final composition of these precipitates does not favor the theory that potassium ferrocyanide is merely dragged down.

The results obtained when cadmium was in excess in an ammoniacal solution were so extraordinary that they deserved further study. The precipitate  $G'''$ ,  $K_2Cd_4(Fe(CN)_6)_3$ , was treated seven times with strong ammonia (sp. gr. 0.90) to see whether a change could be effected by a difference in solubility in ammonia as the  $K_2CdFe(CN)_6$  seemed the more soluble. In this way, a creamy white residue was obtained which gave on analysis  $Fe : Cd :: 1 : 1.99$ , showing  $Cd_4Fe(CN)_6$ , which was also obtained in  $G$  after rewashing with ammonia.

This result, together with the fact that the portion first obtained by decantation when the precipitate was originally treated with ammonia, gave a ratio of  $Fe : Cd$  of exactly  $1 : 1$  shows that the original precipitate can be resolved into the two simple ferrocyanides  $Cd_4Fe(CN)_6$  and  $K_2CdFe(CN)_6$ , and affords important confirmation of the theory that these complicated precipitates are mixtures, advanced several years ago in connection with the ferrocyanides of zinc and manganese.<sup>1</sup>

Now, if this is true for the precipitate in an ammoniacal solution, it ought also to be true of those more complicated ones formed in acid solutions; accordingly,  $C'''$ , which gave  $1 : 1.07$  when freshly precipitated, was treated in the same way with strong ammonia, and the residual cream-colored portion analyzed. This gave a ratio of  $1 : 1.90$ , showing that the same change had taken place, though it was not entirely complete.

To test this further, precipitate  $A$  (neutral, cadmium in excess, made June, 1900) was treated eight times with strong ammonia and the residue analyzed. This gave the ratio of  $1 : 1.99$ , agreeing almost perfectly with  $Cd_4Fe(CN)_6$ .

In order to ascertain whether the change which takes place on standing can be hastened by heating, the precipitate  $E'''$  (acetic, cadmium in excess), which when washed quickly and analyzed gave a ratio of  $1 : 1.07$ , was heated with water containing acetic acid on a water-bath for three days and then analyzed. The result was  $Fe : Cd :: 1 : 1.40$  compared with  $1 : 1.383(E')$  after standing six months in the cold and  $1 : 1.392(E)$  after one year.

This precipitate ( $E'''$  after heating) was next treated eight

<sup>1</sup> This Journal, 19, 556 (1897).

times, with strong ammonia, and the residual portion analyzed. The result was  $\text{Fe} : \text{Cd} : : 1 : 1.97$ , showing again the presence of the normal cadmium ferrocyanide.

These experiments show that the ferrocyanides undergo a change in composition after precipitation which progresses to the same point under the same conditions and which is hastened by heating. The action of ammonia on these precipitates (cadmium in excess) has been confirmatory of the idea that they are either mixtures or else very easily decomposable double salts made up of  $\text{K}_2\text{CdFe}(\text{CN})_6$  and  $\text{Cd}_2\text{Fe}(\text{CN})_6$ .

Written in this way the results are expressed as follows :

Character of solution.	Cadmium in excess.	Ferrocyanide in excess.
Neutral.....	$4\text{K}_2\text{CdFe}(\text{CN})_6 \cdot 3\text{Cd}_2\text{Fe}(\text{CN})_6$	$9\text{K}_2\text{CdFe}(\text{CN})_6 \cdot \text{Cd}_2\text{Fe}(\text{CN})_6$
Hydrochloric ..	$14\text{K}_2\text{CdFe}(\text{CN})_6 \cdot \text{Cd}_2\text{Fe}(\text{CN})_6^1$ $4\text{K}_2\text{CdFe}(\text{CN})_6 \cdot 3\text{Cd}_2\text{Fe}(\text{CN})_6$	$\text{K}_2\text{CdFe}(\text{CN})_6$ ....
Acetic .....	$14\text{K}_2\text{CdFe}(\text{CN})_6 \cdot \text{Cd}_2\text{Fe}(\text{CN})_6^1$ $3\text{K}_2\text{CdFe}(\text{CN})_6 \cdot 2\text{Cd}_2\text{Fe}(\text{CN})_6$	$\text{K}_2\text{CdFe}(\text{CN})_6$ ....
Ammonia .....	$\text{K}_2\text{CdFe}(\text{CN})_6 \cdot \text{Cd}_2\text{Fe}(\text{CN})_6^1$	$\text{K}_2\text{CdFe}(\text{CN})_6$

It would be premature to advance these formulas as representing relations of these complicated and variable precipitates, but the facts seem to warrant this as a working hypothesis, to be used in a further study of the other insoluble ferrocyanides.

Although the results are not all that are desired, many of the precipitates are so easily oxidized, readily decomposed and impossible to filter, that it seemed very doubtful whether any better results could be obtained if the work were repeated.

On comparing the results obtained on cadmium with those on zinc previously published<sup>2</sup> and with those of Stone and Van Ingen<sup>3</sup> we see some cases of remarkable agreement as well as some discrepancies, but a discussion of these results is postponed as it is proposed to continue this work by a similar investigation of the ferrocyanides of the other metals of the periodic group containing cadmium and zinc and also of the analytical group containing zinc, manganese, nickel and cobalt so that, taking zinc as a starting-point, we can see whether the variations in composition have any connection with the analytical grouping or the periodic law and also possibly obtain more knowledge of their constitution.

QUANTITATIVE LABORATORY,  
July 31, 1901.

<sup>1</sup> Freshly precipitated.

<sup>2</sup> This Journal, 19, 547 (1897)

<sup>3</sup> *Ibid*, 19, 542 (1897).

**PROXIMATE ANALYSIS OF SPENT ALKALINE LIQUOR  
FROM THE REDUCTION OF POPLAR WOOD FOR  
PAPER STOCK, BY THE SODA PRO-  
CESS, WITH A DESCRIPTION  
OF THE METHOD.**

**BY MARTIN L. GRIFFIN.**

Received November 17, 1901.

**S**O far as I know, no attempt at analysis of this complex liquid has ever been made, and I know of no references in literature relating to its composition. I have, at different times, made determinations of some of the constituents of this liquor, particularly the total alkali and acetic acid, but this is my first attempt at an investigation of the proximate constituents. The reason why the subject has not been taken up by technical chemists, employed in the paper industry, is because of the complex nature of this waste and the fact that manufacturers have had no idea that it contained anything valuable which they could recover except the alkali, for which greatly improved machinery has been contrived during the past fifteen years.

My interest in this subject was much increased by the action of the Scottish Paper Makers Association, which nearly two years ago offered prizes for the investigation of various waste products resulting from their paper industry, among which was the waste alkaline esparto liquor.

The subject is brought before you now simply in introductory form, but still in a way which I trust will be of some interest and value.

**THE PROCESS BY WHICH THE SPENT LIQUOR RESULTS.**

We are told that M. Meliner, a Frenchman, in 1865, was the first to discover the process of reducing spruce and poplar woods to paper stock by treatment with alkalies under steam pressure. The process now consists in cutting the wood into chips, the fiber of which is about  $\frac{1}{4}$  inch long, and charging same into digesters holding from 3 to 5 cords. Strong sodium hydroxide liquor, containing from about 90 to 100 grams of soda-ash per liter, is then furnished to an amount of about 4 gallons to each cubic foot of capacity of the digester. Steam pressure of 100 to 120 pounds is then applied for from seven to eight hours, when the

mass is blown out under pressure and washed. This alkaline liquor, with the extracted matter, is the subject for our consideration. Before it is exposed to the air, it has a light rose tint, but afterward becomes black instantly. As it comes from the digester, it has a specific gravity of about 1.08 (or 10 $\frac{1}{2}$ ° Bé.) at 15°, and contains 14 to 15 per cent. of total solid matter at 100°, which is very deliquescent.

No attempt at recovering any useful products other than soda-ash has ever been made by those employed in the paper industry, and I doubt if any products as valuable as the ash could be obtained unless it included it. Neither could other valuable products be sought at the expense of the alkaline carbonates.

I submit the following proximate analysis of this liquor. The results are given on the basis of total solids dried at 100°:

	Per cent.
Silica.....	0.11
Iron and aluminum oxides.....	0.02
Calcium oxide.....	0.05
Magnesium oxide.....	0.00
Potassium oxide.....	0.69
Sodium oxide.....	25.69
Carbon dioxide.....	3.43
Absolute acetic acid.....	9.89
Organic matter extracted by naphtha, boiling under 60°.....	1.56
Ether.....	7.14
Absolute alcohol.....	23.26
Water.....	17.02
Total alkalis estimated with normal acid by incineration of the evaporated liquor...	44.25

No attempt is made at combining the acid substances with the bases, though, of course, we know that the carbonic and acetic acids, also the acid resinous substances, are combined with the small amounts of mineral bases, and the alkalis. The remaining 6 per cent. is not definitely accounted for. It is probably all water, largely contained in the sodium hydroxide remaining after saturating all the acid substances, and not accounted for above, and a little water not driven off at 100°.

We know that a large fraction of the total organic matter possesses acid properties, since approximately 18.59 per cent. of the total solids, or 34.43 per cent. of the total organic matter may be precipitated with a slight excess of sulphuric acid at a temperature

of about 40°. This temperature was found best adapted for the precipitation and the washing of the precipitate. At much higher temperatures, the resinous substances will melt, and are more soluble in the menstruum from which they are precipitated. By neutralizing with normal hydrochloric acid, 17.96 per cent. was precipitated.

I hope to be able to investigate chemically and for technical uses, the nature of these acid resinous substances, and present the results at some future meeting.

The method employed for the organic part of this work is the system of solvents recommended by Dragendorff. A quantity of the liquor was contained for use in a tight jar. The total solids were first determined, so that when, for the purpose of different determinations, a definite volume was taken, the solids could be calculated without the trouble of weighing.

In order to prepare a sample suitable for the process of extraction successively by solvents, 5 cc. of the liquor, just neutralized with normal sulphuric acid, were absorbed upon an Adams' paper coil and placed in an extraction thimble for convenience, and dried thoroughly at 100°. The coil was then extracted with naphtha, boiling under 60° in a Soxhlet tube, and the extracted matter determined in the usual way. After the evaporation of this solvent, the coil was successively extracted with ether and absolute alcohol in the same manner. The extract by water contained not only all the organic matter soluble in it, but all the mineral constituents, as sulphates, with the possible exception of traces of silica.

From this extract the organic matter was determined by burning off, and from the mineral portion the alkalies were estimated. The total acetic acid was determined by taking 100 cc., acidifying with slight excess of sulphuric acid, and distilling with the addition of fresh portions of water, until the total distillate amounted to 1 liter. This was distilled a second time to the same volume and the distillate was thoroughly tested for the presence of acetic acid and no other, which was then determined from an aliquot part with tenth-normal sodium hydroxide.

The mineral analysis was made by evaporation and incineration of a fresh sample of 25 cc. in the usual way.

It is the purpose of the writer to pursue this investigation further by taking the extract by each solvent and differentiating it

as far as possible into its separate constituents in the hope that the results may be of some interest, though having no commercial value. The author will be glad to have the subject discussed by the Society, and thankful for any criticisms or suggestions regarding the work.

### DOES "ARGEMONE MEXICANA" CONTAIN MORPHINE?

By J. O. SCHLOTTERBECK.

Received October 24, 1901.

MEXICAN or prickly poppy, as this plant is more familiarly known, is native to the southern states of North America, Mexico, and the West Indies, but it has spread to the north and has also been accidentally introduced by trading ships into distant tropical and subtropical lands to such an extent that it has become a troublesome weed in some localities. The plants are easily propagated from seeds which have for some time been offered by seedsmen for ornamental planting, consequently the prickly poppy has become rather cosmopolitan. The plant is striking in appearance, attains a height of 2 feet, is erect, bristly, and glaucous. The leaves are alternate, sessile, sinuately lobed, armed at the margin and under surface with very sharp prickles. The upper surface of the leaves is beautifully blotched with white. The solitary flowers are yellow, about  $1\frac{1}{4}$  inches broad, possessing a soft, bristly ovary with 4 to 6 red-tipped stigmas. When about to dehisce, to discharge the numerous finely pitted black seeds, the prickly capsule turns from green to brownish-black. When bruised, all parts of the growing plant exude a yellow, milky juice which is acrid, bitter, and of penetrating odor.

The Spanish claim emetic properties for the seeds and purgative properties for the fixed oil therefrom. Others believe the plant to possess narcotic qualities. The juice of the leaves has gained a reputation among the laity, at least, in the treatment of opacities of the cornea, pain of cephalalgia and inflammation of the eyes. Prickly poppy is official in the "Mexican Pharmacopoeia," and while reports upon its therapeutic value are very contradictory and at times fabulous, its importance has merited detailed notice of its properties and uses in the dispensaries of the United States. Considering the repute in which this plant has been held as a remedial agent among Spanish-American peoples it is rather remarkable that so little attention has been directed to its chemical study.

Charbonnier<sup>1</sup> made a chemical study of the leaves and capsules, and the oil of the seeds, and reported the presence of morphine. This statement has never been disputed, being still quoted in reference books to the present day. In 1877 Andrés Ortega published in the proceedings of the Escuela Nacional de Medicina de Mexico his results obtained with several species of Argemone, one of which was the plant under discussion. He operated upon 4 grams of the inspissated juice obtained by incising the unripe capsules and claims to have positively identified morphine. The only other study of this plant was made by Peckolt,<sup>2</sup> who says that the plant is a very popular remedy in Brazil, for almost all known ailments, but that it is not at all prescribed by physicians. He separated a white alkaloid and named it argemonine. The quantity obtained was so small, however, that he could make no study of it.

The very sparse and unsatisfactory information upon the alkaloidal constituents of this plant led the writer to undertake a chemical examination with large quantities of authentic material. One-half of the drug, about 20 pounds, was collected for the writer in Kansas, and the dried whole plants carefully inspected for foreign material. It was found to be free from admixture. An equal amount was grown in the university gardens. At flowering time it was collected, dried, ground, and extracted by the writer so that there seemed to be no possibility of contamination by other alkaloid-bearing drugs.

The ground plant was moistened with very dilute ammonia water and spread out in a thin layer to dry at ordinary temperature. The dry material was extracted in a large copper apparatus with chloroform until exhausted of alkaloid. The deep-green percolate was distilled for recovery of chloroform and the fatty residue digested with several portions of acidulated (acetic acid) water on the water-bath until practically no more color was extracted. The aqueous liquid was concentrated to small volume at low temperature, filtered, and set aside to cool. In a short time the deep yellow liquid had separated a magma of fine yellow needles which looked very much like berberine. It was collected on a filter and recrystallized from water several times. In its behavior with solvents and reagents, and in its physical properties,

<sup>1</sup> *J. de Pharm.*, (5), 7, 348 (1868).

<sup>2</sup> *Ber. d. pharm. Ges.*, 8, 286.

it was identical with berberine. Chlorine water produced with a solution of this compound the characteristic blood-red color that distinguishes berberine. Potassium iodide precipitated a hydriodide completely, leaving a colorless filtrate as is the case with berberine. Finally an acetone compound was made according to the directions of Gaze,<sup>1</sup> and the same quantitative yield obtained. Certainly these qualitative tests amply justify the assertion that this yellow alkaloid is none other than berberine.

Since the presence of berberine in one of the Papaveraceae is rather unusual it was feared that in spite of the great precautions taken, some berberine-bearing drug might have been accidentally mixed with the original, although the amount of berberine separated precluded any such possibility. To make doubly sure, however, just one very large plant that had been hung in the drying room as a museum specimen was employed for a confirmatory examination. This was ground, moistened with ammonia, dried and extracted with absolute alcohol in a liter Soxhlet apparatus. The greenish filtrate after concentration and cooling separated needles of potassium nitrate. After removing all the alcohol the residue was digested with small amounts of acidulated water, the liquid filtered and set aside to evaporate spontaneously. After several days yellow crystals, answering all the well-known tests for berberine, had separated.

The filtrate from the original magma of yellow crystals was concentrated, a second small crop of berberine salt removed, then made alkaline with potassium hydroxide and shaken out several times with ether. The several ethereal portions were filtered, reduced to small volume by distillation and then set aside in an Erlenmeyer flask. In the course of a few days small whitish warts began to accumulate on the side of the flask. After the ether had practically evaporated, the warts were dissolved in acetic acid, diluted with water, made alkaline, and shaken out again with ether. This was set aside as before and after repeating the operation several times the product became white and assumed the form of warts and small prisms, which melted at about 204°. Sulphuric acid gave a violet-red color with a fragment of the alkaloid upon a white slab. Erdmann's reagent gave a deep violet-blue. A beautiful green color was obtained when a little more nitric acid was added to Erdmann's reagent. The quantity

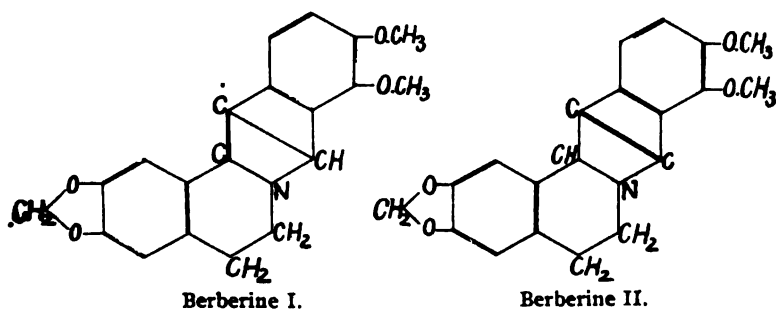
<sup>1</sup> *Arch. d. Pharm.*, 228, 607.



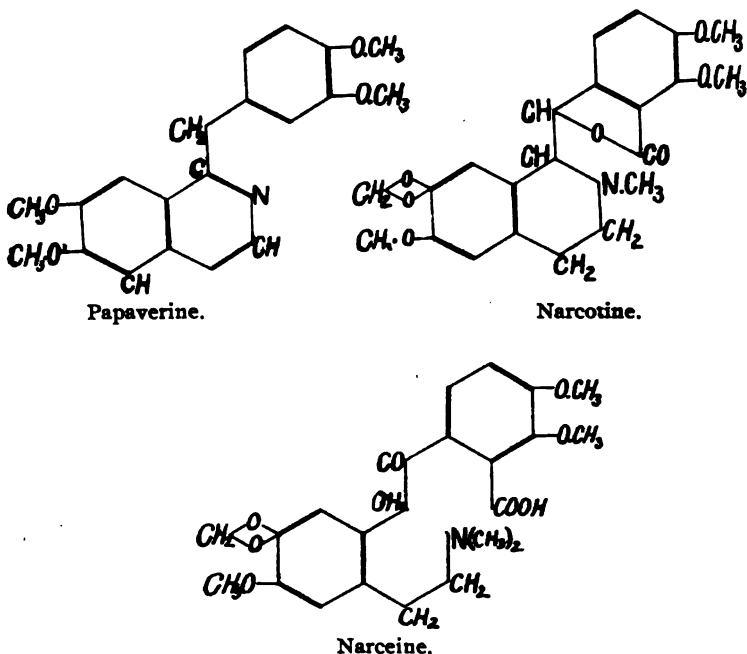
of the alkaloid was too small to admit of further examination but the qualitative tests mentioned together with the experience of the writer with this substance left no doubt that it was the alkaloid protopine. It is doubtless the same alkaloid which Charbonnier and Ortega imperfectly separated and called morphine. Although the color tests are not exactly the same as Peckolt obtained with his argemonine there is no question that it was protopine he had in his hands and not a new alkaloid.

The original drug marc, after having been extracted with chloroform, was percolated with hot distilled water for the purpose of removing the ammonium salts of the acids combined with the alkaloids in the plant. The dark-colored percolate was reduced to a small volume on the steam-bath and set aside to cool. A large crystalline deposit accumulated in the bottom of the vessel. This was collected upon a Buchner filter and thoroughly washed with cold water. Much of the brownish coloring-matter was removed in this manner. The residue when dry was grayish in color. It consisted partly of calcium phosphate. The acids in combination with the alkaloids have not been identified with certainty. This will be left for a future paper.

At first thought the presence of berberine in the Papaveraceae weakens the position held by the writer and others that botanical relationship to a great extent predicts chemical relationship. A comparison of the structural formulas of berberine submitted by Perkin<sup>1</sup> with those of the opium alkaloids papaverine, narcotine, and narceine, demonstrates conclusively that the discovery of berberine in a plant of the poppy family strengthens rather than weakens this position.



<sup>1</sup> *J. Chem. Soc.*, 1, 991 (1890).



These four alkaloids together with hydrastine constitute the isoquinoline group of plant alkaloids. They are, with the exception of narceine, distinct derivatives of the parent base isoquinoline as is shown above. Narceine shows very close relationship to the same base. By the constitution of the above-named bases occurring in the poppy family, the botanico-chemical principle spoken of is graphically enunciated.

#### SUMMARY.

1. *Argemone Mexicana* does not contain morphine.
2. The alkaloids of *Argemone Mexicana* are berberine and protopine.
3. The argemonine of Peckolt is protopine.
4. Potassium nitrate is one of the salts existing naturally in the plant.

In conclusion I wish to express my thanks to Mr. C. W. Johnson, who kindly assisted me in this investigation.

SCHOOL OF PHARMACY, UNIVERSITY OF  
MICHIGAN, ANN ARBOR, MICHIGAN.

## DETERMINATION OF MANGANESE IN IRON.<sup>1</sup>

BY WILLIAM A. NOYES AND G. HARRY CLAY.

Received November 1, 1901.

THE process here described involves no new principle. It is a combination of several different processes and, so far as we are aware, has not been used before.

### REAGENTS.

*Ferrous Ammonium Sulphate.*—Dissolve 8.56 grams crystallized ferrous ammonium sulphate in water containing 40 cc. of dilute sulphuric acid (25 per cent.), and make to 1 liter.

*Potassium Permanganate.*—A standard solution of such strength that 1 cc. is equivalent to about 0.001 gram iron. The manganese equivalent for the present method is found by multiplying the iron equivalent by  $\frac{43}{111}$ .

*Sodium Acetate.*—Thirty grams of crystallized sodium acetate, 30 cc. of acetic acid (30 per cent.), and 170 cc. of water.

*Bromine Water.*—A saturated solution.

Dissolve 1.5 grams of the sample in 25 cc. of nitric acid (sp. gr. 1.20), or in 20 cc. of nitric acid and 5 cc. of hydrochloric acid, (sp. gr. 1.12). Heat till dissolved, transfer to a 300 cc. flask, add a solution of sodium carbonate till nearly neutral, and then an emulsion of zinc oxide slowly till the precipitate of ferric hydroxide forms. After two minutes add an excess of zinc oxide.<sup>2</sup> Make up the volume to 300 cc., mix by pouring back and forth into a dry beaker, and filter through a dry filter.

Take 200 cc. of the filtrate, add 20 cc. of the solution of sodium acetate and 40 cc. of bromine water. Heat nearly to boiling, stirring occasionally and adding more bromine water, if necessary, till the precipitate of manganese dioxide separates. Filter and wash. The precipitate adhering to the beaker need not be removed, but the beaker must be rinsed thoroughly. Place the beaker under the funnel containing the precipitate and drop upon the latter, from a burette, the solution of ferrous ammonium sulphate till solution is complete. During this operation break up the precipitate occasionally with a fine stream of water from a wash-bottle. Unless the manganese exceeds 0.4 per cent., not more than 20 cc. of the solution should be used.

<sup>1</sup> The work here described formed the basis of a thesis for the degree of Bachelor of Science at the Rose Polytechnic Institute.

<sup>2</sup> Geo. Auchy: This Journal, 18, 998.

Wash out the filter and titrate the filtrate with the standard permanganate solution. The difference between the number of cubic centimeters of permanganate used and the amount which would have been used by the ferrous ammonium sulphate employed, if no manganese dioxide had been dissolved in it, multiplied by the manganese equivalent of the solution, will give the amount of manganese in 1 gram of iron.

In testing the method, considerable difficulty was experienced in obtaining an iron solution free from manganese. All samples of ferrous sulphate and of iron ores which were available contained some of that element. Finally it was found that a sample of ammonia iron alum was free from manganese and by precipitating a solution of the salt with sodium hydroxide, washing by decantation, and dissolving in sulphuric acid a ferric sulphate solution free from manganese was prepared. A manganese solution of known strength was prepared by dissolving a weighed quantity of potassium permanganate in water, just decolorizing with sulphurous acid and making up to a known volume. A quantity of the iron solution containing 1.5 grams of iron was mixed with a measured quantity of the manganese solution and the manganese was determined by the process described above. The results were as follows, stated as per cents. of the iron present.

Manganese taken.	Manganese found.
0.100	0.109
0.300	0.300
0.300	0.300
0.500	0.490
0.700	0.687
0.700	0.681
0.900	0.897
1.100	1.090

To determine whether evaporation with sulphuric acid to expel the nitric acid used for solution, as is done in Volhard's process, is necessary, two samples of iron were analyzed, first by solution in nitric acid followed by evaporation with sulphuric acid, and second by solution in nitric acid and direct precipitation. The results were:

I.	
Nitric and sulphuric acids.	Nitric acid.
0.335	0.344
0.348	0.326
0.332	0.329
<hr/> Mean, 0.338	<hr/> 0.333

## II.

0.392	0.404
0.408	0.412
<hr/>	<hr/>
Mean, 0.400	0.408

It is evident that the evaporation with sulphuric acid is unnecessary and the saving effected here nearly or quite compensates for the extra precipitation as compared with Volhard's method.

As solution is more certain to be complete, for some irons, in a mixture of nitric and hydrochloric acids than in nitric acid alone, Mr. R. C. Warren has made some comparative determinations with these two solvents.

## I.

Nitric acid.	Nitric and hydrochloric acids.
0.189	0.207
0.196	0.213
0.207	0.207
0.210	....
<hr/>	<hr/>
Mean, 0.200	0.209

## II.

0.302	0.306
0.310	0.302
<hr/>	<hr/>
Mean, 0.306	0.304

The precipitation of the manganese dioxide appears to take place a little more easily from the solution in which hydrochloric acid has been used.

The method resembles Volhard's method as described by Blair in his "Chemical Analysis of Iron," more closely than any other. It has the advantage of avoiding the evaporation with sulphuric acid to destroy carbonaceous matter required by that method. It also gives a sharp end reaction. Not only is the end in titrating a neutral manganese solution with permanganate difficult to hit, but it is very uncertain because of the catalytic action of manganese dioxide in causing the decomposition of potassium permanganate.<sup>1</sup>

TERRE HAUTE, IND., October 28, 1901.

<sup>1</sup> Morse, Hopkins and Walker: *Am. Chem. J.*, 18, 401.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE NORTH CAROLINA DEPARTMENT OF AGRICULTURE.]

## NEW APPARATUS.

By CHARLES B. WILLIAMS.

Received November 30, 1901.

### A DEVICE FOR MARKING VOLUMETRIC FLASKS.<sup>1</sup>

It has been the custom in this laboratory for a number of years to graduate or calibrate all volumetric flasks before using, as experience has taught us that the different manufacturers have neither a uniform system nor a constant temperature of graduation. We use as a liter the volume occupied by a cubic decimeter (kilogram) of water at 4° C. *in vacuo*, and graduate all flasks to contain the indicated amounts at 22° C., as this is the mean annual temperature of our laboratory during working hours.

The calibrating apparatus used is that devised by Morse and Blalock.<sup>2</sup> The marker which we have used with such satisfaction for the past year consists primarily (Fig. 1) of a solid iron base *H* supporting a standard *N* of wrought iron. The collars *A* and *S* are fitted to spindle with splines. The set-screws *a* and *c* afford means of clamping the movable carriage *S'* and arm *AB* in various positions in a vertical plane; thus flasks any length up to 50 cm. can be marked. The marking-point *F* is made of steel and fitted into arm *F'*, which has a collar *G*, loose on shouldered collar *M*, and can be easily adjusted to any position.

*C* is made of rubber or cork which can be replaced by removing the thumb nut *e*. The carriage *M''* which supports flasks is made of wood and is screwed to a washer on the spindle of the hand-wheel *S''*. This carriage is constructed to accommodate any sized flask from 50 to 1000 cc. capacity.

The apparatus can be screwed to any secure foundation, as a table or window sill.

In marking, the arm *AB* is elevated to allow the flask to sit upright in the movable carriage *M''*, then the arm is lowered until *C* fits tightly in the neck of the flask when the arm is made fast by the set-screw *a*. By means of the hand-wheel *S''*, the flask carriage and stopper can be revolved horizontally. The arm *F'* may be adjusted so that the marker *F* will just be at the same height

<sup>1</sup> Read before the North Carolina Section of the American Chemical Society, on November 9, 1900.

<sup>2</sup> *Am. Chem. J.*, 16, 479-488.

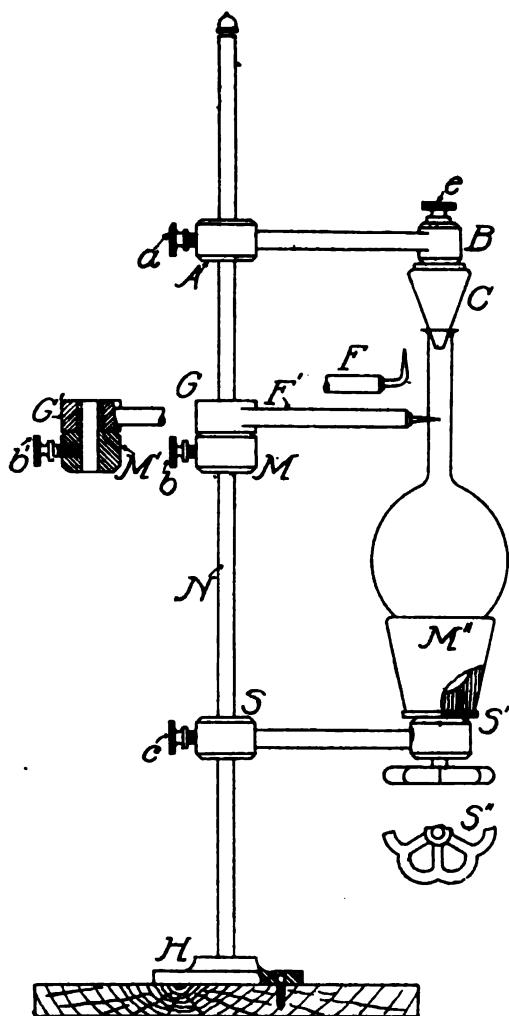


Fig. 1.

as the bottom of the meniscus of the measured liquid in the flask, when the arm  $F'$  can be pressed laterally with the hand and force the marker  $F$  into the beeswax, which has been melted and spread in a thin coating with a camel's hair brush over the neck of the flask where the marking is to take place. Then without relieving the pressure on the marker, the hand-wheel is revolved, which makes a mark around the neck of the flask through the beeswax

at the bottom of the meniscus. This mark is etched into the glass by means of hydrofluoric acid applied with a camel's hair brush and allowed to remain ten or fifteen minutes. With this device and procedure one is enabled to mark flasks very rapidly with but little practice.

#### A MODIFIED BULB TUBE FOR NITROGEN APPARATUS.<sup>1</sup>

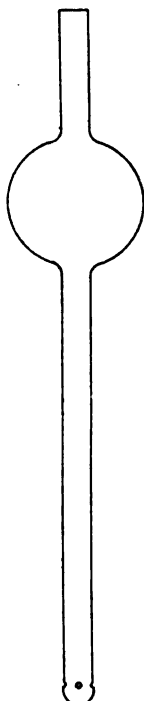


Fig. 2.

This bulb (Fig. 2) is of glass and consists of an upper stem 5 cm. long, a lower one 18 cm. long, and a bulb 5 by 5 cm. The bore of the stem is 7 mm. and thickness of walls about 1 mm. The free end of the lower stem is closed to a 2 mm. hole. Above this hole 6 or 7 mm., are arranged circularly around the tube four holes (diameter 2 mm.) equidistant apart. It is the experience in this laboratory that in using the plain open-end bulb tube with materials rich in nitrogen, such as sodium nitrate, cotton-seed meal, blood, etc., there is often loss of ammonia by non-absorption by the standard acid, as, at the beginning of the boiling, ammonia is copiously evolved and forced into the acid through one large orifice, hence coming in contact with only a small volume of the acid solution.

With this tube the ammonia is forced into the acid through five openings in as many different directions, thereby giving ample provision for complete absorption. It has now been in constant use for over fourteen months with perfect satisfaction, even in high-grade ammoniated materials. When distillation is complete, the tube is disconnected from the nitrogen apparatus and is used to stir the solution in titration.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY, UNIVERSITY OF MICHIGAN.]

#### A ROTARY CEMENT KILN FOR USE IN THE LABORATORY.

BY E. D. CAMPBELL.

Received January 6, 1902.

**I**N the researches on the constitution of hydraulic cements which were begun in this laboratory about three years ago, the cements under examination were prepared in small crucible

<sup>1</sup> Read before the North Carolina Section of the American Chemical Society, on November 23, 1901.



furnaces, heated with gasoline. The material being burned, was formed into round or oval disks, and gradually raised during a period of three or four hours to the desired temperature, this latter being determined by means of three LeChatelier thermocouples passed through the walls of the furnace, and brought close to the material under treatment. This method of burning produces a clinker similar in appearance and properties to that burned in large fixed kilns. As the investigations progressed it soon became evident that time as well as temperature and chemical composition of the mixture was an important factor in determining the constitution of the resulting clinker. If then reliable knowledge regarding the constitution of cements produced by a modern rotary process was to be obtained, it became necessary to devise a small rotary, in which cement could be produced and in which the temperature and the time during which the material was heated, were under control. The small rotary which has been in use during the past year in this laboratory, has given such satisfactory results, that we have thought a description of the same would not be without interest to those engaged in studying the physics and chemistry of hydraulic cements.

The rotary proper consists of a piece of 8-inch (20 cm.) steam pipe 32 inches (81 cm.) long, provided with a collar and two shallow grooves turned to run on friction wheels attached to a cast-iron base having four long set screws for legs, by means of which the pitch of the rotary may be regulated. The rotary has attached to it the rim of a large 30-tooth sprocket wheel. The lining of the rotary was made of four sections of hard burned magnesite tubes. The tubes, two of which are shown at A in the cut, are 3 inches (7.5 cm.) inside and 6 inches (15 cm.) outside diameter, and 8.5 inches (21 cm.) long, and so shaped that when placed end to end they form a smooth joint inside and out. These tubes were molded under hydraulic pressure in special dies made for this work. The molding and burning was done by Harbison and Walker, of Pittsburg, Pa., who used the same material as they employ in the manufacture of magnesite bricks. In lining the rotary the magnesite tubes were supported concentric with the steel jacket and the annular space between the tubes and the jacket was filled with asbestos. At the ends of the magnesite tube S for a distance of about 2 inches, the asbestos was mixed with raw and burned fire-clay and sodium silicate, the

mixture and asbestos being firmly tamped to prevent any displacement of the magnesite tubes during rotation.

The tube is turned by means of a  $1/7$  H. P. electric motor, B, the speed being reduced by means of the pulley and worm gear C. The worm gear is connected by means of a sprocket chain to the sprocket wheel on the rotary, the gearing being so planned that the tube requires about one minute and twenty-five seconds to make a single revolution.

The heating of the tube is done by means of a Hoskins hydrocarbon burner supplied with low-boiling gasoline from a tank situated some distance from the furnace. A working pressure of from 50 to 60 pounds per square inch in the gasoline tank gives the most satisfactory results.

The temperature of the tube is controlled by means of a Le-Chatelier thermocouple, D, connected to the reflecting galvanometer E. In order to protect the wires of the thermocouple they are passed through a double-bored porcelain tube 7 mm. in diameter, which tube is covered for a distance of about 8 inches with platinum foil. It was found necessary to protect the porcelain tube in this way with platinum in order to avoid the slagging of the porcelain through contact with the basic clinker. The cold junction of the couple is maintained at  $0^{\circ}$  C. by immersion in a small beaker which is kept filled with ice during an experiment. This small beaker is contained in the larger beaker F, from which it is insulated by means of a thick felt packing.

A number of experiments were made to determine the temperature of the inside of the furnace at different points. This was done by constructing a special thermocouple insulated in double-bored porcelain tubes long enough to reach the entire length of the furnace when inserted at the cooler or feed end. A series of experiments demonstrated that the temperature attained its maximum at a zone about 6 inches (15 cm.) from the hot or discharge end. From the hot zone the temperature falls off regularly to the cool or feed end. The fixed couple D projects about 3.5 inches (8.7 cm.) into the hot end of the furnace. At this point the temperature averages about  $40^{\circ}$  C. lower than at the hot zone, but on account of the intense heat at this latter point and the length of the porcelain tube required to reach it, it was found impracticable to keep the couple at this point, as the tubes would invariably sag and break after a comparatively short ex-

posure. The same difficulty of sagging and breaking of porcelain tubes was experienced to a much greater degree during the measurements of temperature along the axis of the furnace, so that after the general distribution of heat was determined in a number of cases, it was not deemed necessary to use anything but the short fixed couple to control the temperature. The temperatures found at one series of measurements were as follows: At the fixed couple  $1460^{\circ}$  C. ( $2660^{\circ}$  F.); 6 inches (15 cm.) from the hot end  $1500^{\circ}$  C. ( $2732^{\circ}$  F.); 8 inches (20 cm.) from hot end, end of section 1,  $1487^{\circ}$  C. ( $2709^{\circ}$  F.);  $12\frac{1}{4}$  inches (31 cm.) from hot end, middle of section 2,  $1414^{\circ}$  C. ( $2577^{\circ}$  F.); middle of furnace, end of section 2,  $1392^{\circ}$  C. ( $2538^{\circ}$  F.); middle of section 3,  $1335^{\circ}$  C. ( $2435^{\circ}$  F.); end of section 3,  $1286^{\circ}$  C. ( $2347^{\circ}$  F.); temperature of escaping gas at feed end of furnace,  $1200^{\circ}$  C. ( $2192^{\circ}$  F.). While the above figures show the distribution of heat within the furnace, they do not show the maximum temperatures attainable. The temperature of the hottest section (section 1) of the furnace has been raised  $130^{\circ}$  C. higher than the above figures, or to nearly  $1630^{\circ}$  C. ( $2966^{\circ}$  F.) at the hot zone. This is enough to give perfectly sound clinker from the most refractory materials and is too high for most mixtures.

In making an experimental burning the furnace is lighted and the galvanometer observed until the deflection shows that the desired temperature has been reached, the time required to bring the furnace to the working temperature being usually from forty-five minutes to one hour from the time of lighting. When the furnace has attained the desired heat, feeding of the prepared slurry is begun. When the furnace is working, the discharged end is closed by means of the bricks G suitably cut to admit the flame into the furnace and the clinker to drop into the asbestos-lined box H placed to receive it. The feed end of the furnace is partially closed by a brick with a shallow trough cut into it, serving to guide the prepared slurry into the furnace and a small pile of slurry is maintained at the feed end of the furnace, being replenished as fast as the material works down through the tube. With one revolution in one minute and twenty-five seconds, and a 6 per cent. pitch to the tube, the time of passage is from twenty-five to thirty minutes. During the first hour of feeding from 1,500 to 1,700 grams of prepared slurry can be fed, and after the

first hour from 1,000 to 1,200 grams per hour. This yields from 600 to 700 grams of clinker per hour from the time when the first pieces of clinker appear to the time feeding is stopped. The last material fed does not come through the furnace in less than forty-five minutes on account of there being nothing back of it to push it forward. When the first clinker has made its appearance, it may be examined, and if it seems overburned or underburned, the temperature can easily be lowered or raised, until the clinker has the desired appearance. When once the clinker shows the desired appearance the temperature can be maintained so as not to vary more than  $10^{\circ}$  during the entire run. The uniformity of temperature produces a corresponding uniformity in the resulting clinker, thus enabling the influence of temperature upon the resulting clinker to be easily studied.

In preparing the slurry for burning, the method employed will depend upon whether the conditions to be studied are those found in the "wet" or "dry" process. If it is desired to imitate the conditions found in the wet process, the marl or limestone used is dried and ground to practically all pass through a 100-mesh sieve and the clay or shale is also dried or ground, if necessary. After the necessary analyses have been made, weighed portions of the clay or shale with the marl or limestone are thoroughly mixed with sufficient water to give a liquid slurry containing from 40 to 50 per cent. of water. This liquid slurry is evaporated down with frequent stirring until it has the proper consistency to work well. After evaporating and cooling, the slurry is thoroughly worked up and rolled out by means of an ordinary rolling-pin on rectangular pieces of galvanized iron, which can be placed in a drying rack, J. After rolling out to a thickness of  $1/4$  to  $3/8$  inch on these shelves, the slurry is cut by means of the thin cutting wheel, I, passed longitudinally and transversely so as to produce small cubes of approximately the same size, and when all the material has been rolled out and cut in this way, the shelves are put into the drying racks J, and thoroughly dried. After drying, the slurry is easily removed from the shelves, and the cubes separated by hand. The time required for rolling out and cutting about 4,500 grams need not exceed thirty minutes. About 4,500 grams of dried material are usually used, as this will yield from 2,500 to 2,800 grams of perfectly uniform clinker, the loss being very small during the work.





When the conditions of the dry process are under examination, the dried materials, clay or shale with marl or limestone, are mixed and well ground together in a laboratory jar mill. The mill at present in use, which has given very satisfactory results in grinding both raw material and clinker, was furnished by the Bonnot Co., of Canton, Ohio. After mixing and grinding dry, the material is moistened with just enough water to enable it to be rolled out and cut up like that used for the wet process.

ANN ARBOR, MICH.  
December 16, 1901.

### THE ALLOYS OF ALUMINUM.<sup>1</sup>

BY WILLIAM CAMPBELL AND JOHN A. MATHEWS.

Received December 7, 1901.

THE fact that aluminum can now be classed as one of the common metals, since it can be obtained at a moderate price, and of certainly as great purity as other commercial metals, has of late years made it the subject of many researches. Its alloys with nearly all the commoner metals have been made or attempted, but their adaptability to commercial uses has rested solely upon the ordinary tests and many statements of a very unscientific nature have been published about them.

While working in Professor Sir William Roberts-Austen's laboratory, at the Royal College of Science, the authors were engaged in examining anew some of these alloys in the light of recent advancement in those methods of alloy research which Professor Roberts-Austen has done so much to promote. Through the interest in our work which he exhibited and by means of the facilities which he provided us for carrying on metallographic and pyrometric observations we now have the honor to present the following results,—not as a completed investigation, but as the beginning of one which has, of necessity, been transferred from one laboratory to another. We expect to continue work upon some of these lines in the metallurgical laboratory of Columbia University. It has been thought best, therefore, to present the results already obtained by us in the laboratories at South Kensington in the following paper.

Professor Richards, whose researches upon the industrial applications of aluminum are so well known and which entitle him to be considered as the foremost authority upon the metallurgy of

<sup>1</sup> Read before the New York Section of the American Chemical Society, November 1, 1901.

aluminum and its alloys, has given us a very valuable work on the subject in his book, "Aluminum: Its History, Properties, Metallurgy, etc." In so far as this book deals with industrial topics, resting upon Professor Richards' own authority, it is no doubt the best source of information to be had. A great deal of what might be called the "pure science" of the book—particularly in regard to the alloys—is decidedly at fault and should be revised thoroughly, and many portions, almost without exception direct quotations from antiquated sources, might well be omitted.

In classifying the alloys of aluminum, Professor Richards points out that the useful ones fall into two groups.

1. Those in which small amounts of another metal are added to aluminum.

2. Those in which aluminum is added in small amounts to other metals.

Generally speaking the metal present in the smaller amount does not exceed 15 per cent., and practically, in alloys of the first class, much smaller amounts give the maximum improvement in the alloy, hardness being one of the qualities most sought. Aluminum seems to be able to take up considerable quantities of certain metals without undergoing a change in volume, though the density and probably the hardness are improved in such cases.

Aluminum seems to form intermetallic compounds more readily than almost any other single metal unless it be the alkalis. On the other hand, there are several metals with which it will neither combine nor even mix to give homogeneous alloys except when the added metal is present in very small percentages. Of this class of metals we might mention lead, bismuth, and cadmium.

Various workers have mentioned the formation of one or more compounds of aluminum with antimony, chromium, cobalt, copper, nickel, gold, manganese, magnesium, mercury, molybdenum, platinum, titanium, tungsten, and other metals. In the light of recent work we may doubt that the formulas of these compounds have been correctly given in all cases. We are positive that many of the copper-aluminum compounds so-called, that have been mentioned in past years, have no existence. They are neither indicated by metallographic nor pyrometric evidence and the fact that from many alloys of aluminum beautiful and for the most part rather stable crystals can be obtained by the use of proper solvents does not prove that these crystals consist of a single in-



intermetallic compound. Any one who has worked much with such crystals knows that from alloys of different percentage compositions crystals may be isolated which, while entirely identical in form, give very different analyses. The crystals, granting that they contain an intermetallic compound, may also contain one or other of the constituents of this compound in solid solution. This quantity of dissolved substance will be found to increase in amount as we approach the alloy whose percentage corresponds exactly to the formula-percentage of the intermetallic compound under consideration. It seems to have been the custom in the past to assign a formula to all crystalline products which could be isolated from alloys. The result of this method and others equally faulty is that in the literature one may find mention of at least eight carbides of iron, while in iron one finds but one. Similarly, some fifteen compounds of aluminum with copper and nearly as many with molybdenum have been mentioned. Pyrometric evidence indicates but two of the former (Al-Cu), while Le Chatelier thinks he has microscopic evidence of four; certainly the latter figure is the limit. We have not studied Al-Mo alloys.

*Alloys of Aluminum with Lead, Bismuth, and Cadmium.*—Aluminum, like zinc, will not mix in all proportions with lead or bismuth to form homogeneous alloys, but separates into two layers. Unlike zinc, it does not mix in all proportions with cadmium. Dr. Alder Wright has studied several such pairs of metals<sup>1</sup> and his results show that in every case each of the resulting layers of metal consists of a primary constituent holding in solid solution a small amount of the other metal of the pair under examination. Thus lead and aluminum, after heating together, separate into layers, lead, of course, at the bottom containing 0.07 per cent. aluminum, while the upper layer consisted of aluminum containing 1.92 per cent. of lead. Our experiments agree with Dr. Wright's in the main. With regard to the Al-Cd alloys we found the top portion to be aluminum and the base cadmium, but in the cadmium could be seen bright minute crystals, whose specific gravity was less than that of cadmium and hence the crystals were found mostly at the junction between the two layers. The alloy was slowly cooled. According to Wright, cadmium dissolves 0.22 per cent. of aluminum and aluminum dissolves 3.39

<sup>1</sup> *J. Soc. Chem. Ind.*, 1892, p. 492.

per cent. of cadmium when these metals are heated in contact for eight hours at about  $750^{\circ}\text{C}$ .

*Aluminum and Platinum.*—Tissier Brothers state that an alloy containing 5 per cent. of platinum approaches in color gold containing 5 per cent. of silver. We made such an alloy, also one of 10 per cent. platinum, but were unable to detect any change in color. The metals seem to unite chemically and by dissolving away the excess of aluminum, long needle-shaped crystals remained. These gave by analysis, 4.35 per cent. aluminum and 95.65 per cent. platinum, which corresponds closely to the formula  $\text{AlPt}_2$ ; we do not state, however, that such a compound exists. The freezing-point curves of those series of aluminum alloys which have been completely ascertained show that the intermetallic compounds of aluminum are numerous but they also lead us to doubt the existence of many of those which have been mentioned in the past. When platinum is present in large amount, say from 30 to 50 per cent., the alloy is decidedly yellow. Mr. George S. Newth showed us some alloy of this kind made several years ago in the electric furnace. Indeed, the production of this alloy was probably the first instance of a colored alloy from colorless or "white" metals. In this case we may almost assume that the color is an evidence of chemical combination, just as it is in Roberts-Austen's purple alloy,  $\text{AuAl}_2$ . In the formation of this beautiful compound the heat evolved during the reaction is said to be so great that when once the reaction is started it proceeds without application of external heat.

*Aluminum and Tungsten.*—As has been known for a long time, these two metals readily unite. In working with alloys containing from 3 to 17 per cent. tungsten, we obtained in every case except one, large, thin monoclinic crystals. In a single instance some very beautiful hexagonal crystals terminating in hexagonal pyramids were obtained. All efforts to obtain a further production of these crystals were unsuccessful, except that in one alloy both kinds occurred (see Figs. 1 and 2). We were not aware that in the chance production of them in these two cases, any peculiar conditions were operating which were absent in the instances in which only monoclinic crystals resulted. A number of very curious chemical properties were noted in studying these crystals. The analyses resulted as follows:

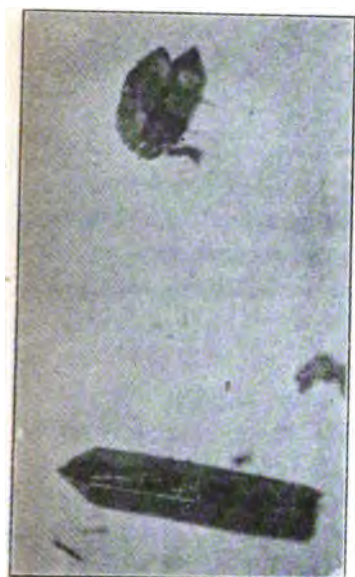


Fig. 1.



Fig. 2.



Fig. 3.

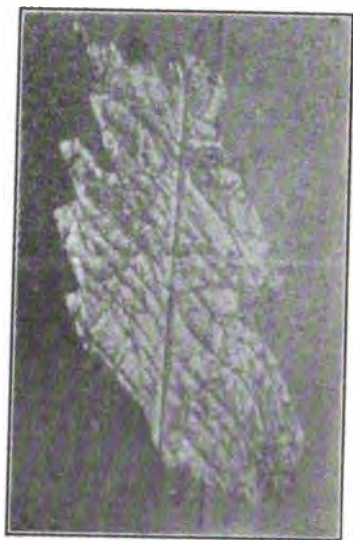
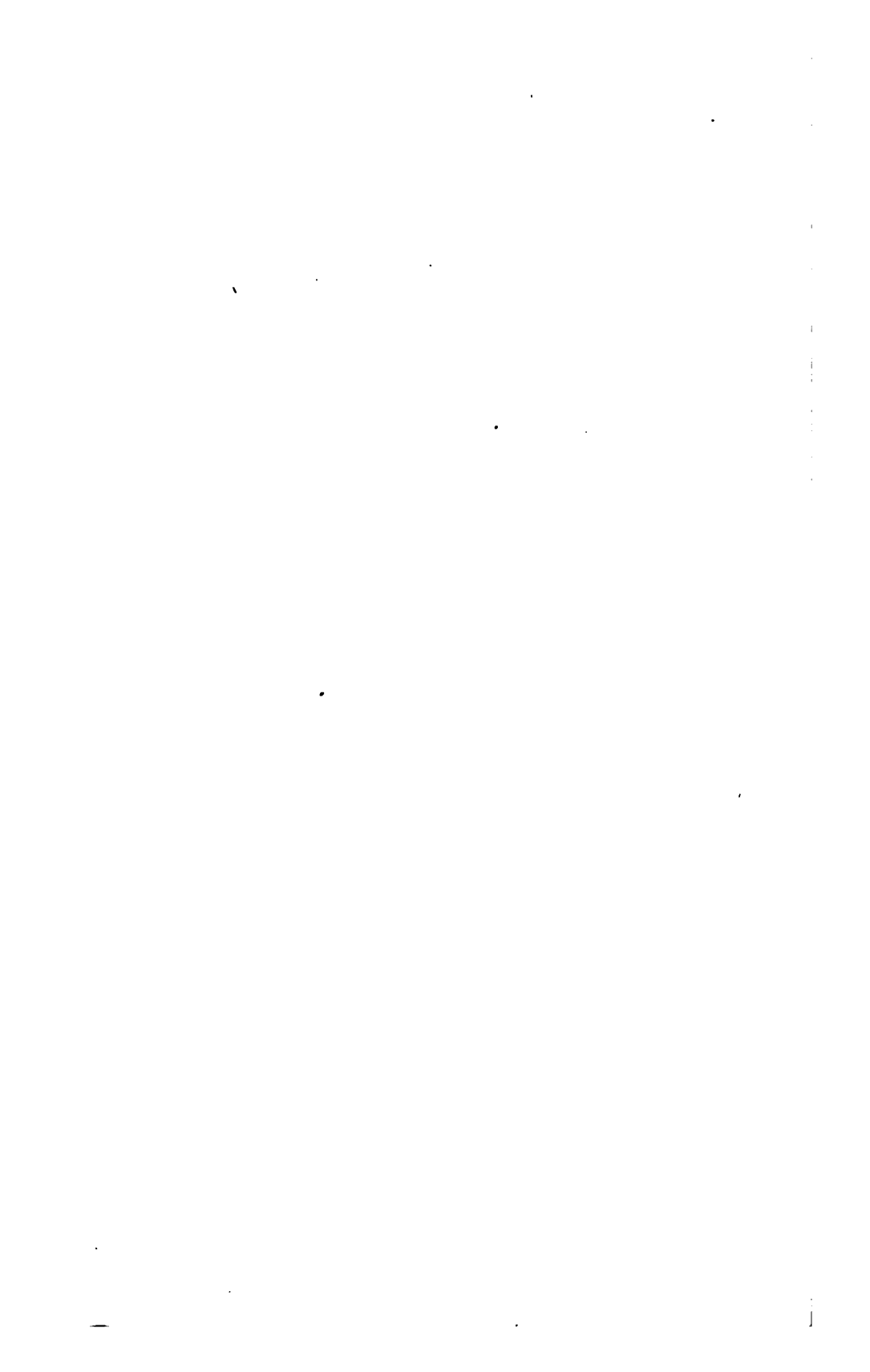


Fig. 4.



Monoclinic crystals.	Tungsten. Per cent.	Aluminum. Per cent.	Possible formula.
Sample 1.....	57.1	....	....
" 2.....	57.97	41.97	$WAl_3$
" 3.....	60.43	39.62	?

The third sample was in the form of very fine siftings and the crystals may have been somewhat acted upon by the dilute hydrochloric acid used in removing the excess of aluminum.

Hexagonal crystals.	Tungsten. Per cent.	Aluminum. Per cent.	Possible formula.
Sample 4.....	50.91	....	....
" 5.....	49.19	50.52	$WAl_3$

Now, whether these are true chemical compounds of the formulas given or not, they certainly differ as distinctly in chemical behavior as they do in crystalline form. The monoclinic crystals are readily attacked by aqua regia, while the hexagonal ones are not. A mixture of nitric, hydrochloric and sulphuric acids is without effect on them and when fused with mixed alkaline carbonate plus a little nitrate in a nickel crucible, the crucible suffered much more than the crystals. With potassium bisulphate they are decomposed with deflagration at a very moderate temperature. We supposed that this fusion would give a mixture of alkali tungstate and aluminate, but were surprised to find that upon treating the fusion with water, a white, more or less flocculent insoluble residue remained. This residue was about as difficult to deal with as the original substance. It was insoluble in aqua regia, slightly soluble in ammonia, but soluble in caustic potash. The monoclinic crystals by fusion with bisulphate gave the same white residue. This we believe is somewhat impure aluminum tungstate,  $Al_2(WO_4)_3 \cdot 5H_2O$ . It loses by ignition 10.4 per cent. water, and one analysis gave 66.3 per cent. tungsten; theory for  $Al_2(WO_4)_3$  requires 69.17 per cent.

*Aluminum and Nickel.*—The most commonly used metal for hardening aluminum is nickel. For this purpose, from 2 to 5 per cent. of nickel is employed, often in conjunction with copper, tungsten, and other hardeners. When the combined percentage of these hardeners is from 7 to 10 per cent., an alloy is obtained which casts exceedingly well and is very tough. We made up alloys containing 2.12, 3.14, 4.15, and 7.97 per cent. nickel. The first of these contained a few bright crystals, while the last consisted of a network of skeleton crystals. On isolating these

by the use of dilute hydrochloric acid, beautiful single crystals were obtained, each crystal being made up of numberless minute dendritic plates. The groundmass in which these crystals lie is isomorphous with aluminum and melts at a slightly lower temperature. An alloy containing 7.97 per cent. of nickel, and a single crystalline mass isolated from it, are shown in Figs. 3 and 4.

*Aluminum and Tin.*—Heycock and Neville, in their work upon the depression of the freezing-point of metals by the presence of other metals in them in solution, state that 0.48 per cent. alu-

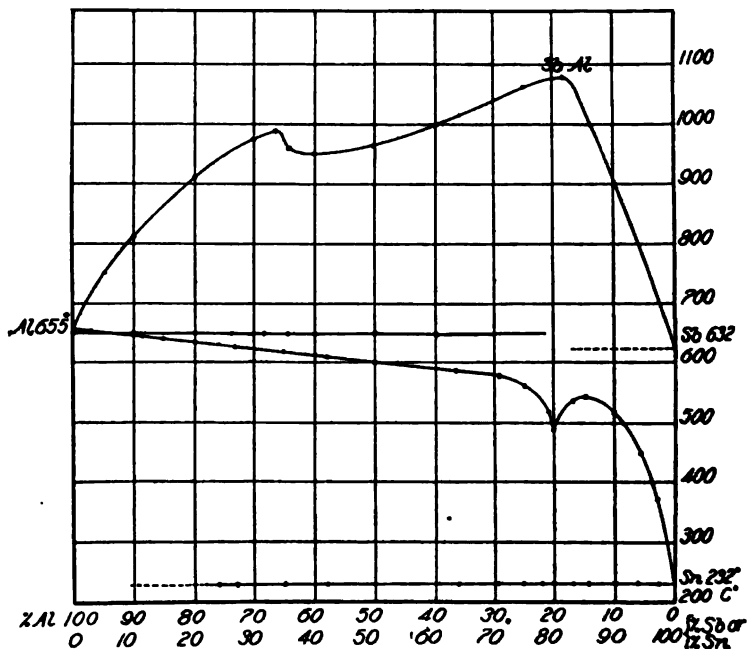


Fig. 5.

minum gives the lowest freezing-point, *viz.*, 3° C. below that of pure tin. Further additions of aluminum to tin cause a rapid rise in the melting-point of the alloy; ten per cent. of aluminum raises the melting-point nearly 300° C. Our own freezing-point curve (Fig. 5) shows that beginning at pure aluminum (m. p., 655° C.) the addition of tin causes a gradual lowering of the freezing-point up to 74 per cent. tin (570° C.), when there is a sudden drop to 80 per cent. tin at 490°, followed by a rise to 85 per cent. tin at 550° and then a regular fall to the eutectic-point,

99.52 per cent. tin ( $229^{\circ}$ ). Microscopic examination of this series of alloys, while not yet completed, shows grains and dendrites of aluminum, or aluminum containing tin in solid solution, in a groundmass of tin (containing 0.48 per cent. aluminum). As the alloys become richer in aluminum, the grains of aluminum increase while the groundmass decreases in amount and disappears altogether at about 90 per cent. aluminum; that is, aluminum containing up to 10 per cent. tin consists of a single solid solution crystallizing isomorphously with pure aluminum. The eutectic<sup>1</sup> in this series of alloys differs apparently from most eutectics in that it has not as yet been resolved into two microscopically visible constituents and, indeed, seems to crystallize isomorphously with pure tin. It seems like a single solid solution rather than two juxtaposed saturated solid solutions of tin in aluminum and aluminum in tin which would be expected from analogy with other eutectic alloys. The idea of either a pure metal or single solid solution constituting a eutectic is not contrary to the definition of a eutectic. We wish to work further on this subject. The meaning of the sudden break in the freezing-point and curve is as yet unsettled. Its existence is even disputed by Anderson and McClean (Brit. Asso., Glasgow, 1901). Gautier's curve, while not identical with ours, does show an irregularity in the symmetry of the curve between 15 and 25 per cent. aluminum. We determined the freezing-points between these percentages in duplicate and upon different series of alloys made by different methods. In all our freezing-point curves, the alloys which we actually examined are indicated in the curves by heavy dots occurring at the percentage composition of the alloys examined. In the same vertical line with these dots, are indicated other breaks occurring in the cooling curves at temperatures below the initial freezing-point.

*Aluminum and Antimony.*—In Richards' "Aluminum" we find a short summary of the conclusions of several workers on these alloys.

Alder Wright<sup>2</sup> came to the conclusion that antimony formed no commercially valuable alloy with aluminum. He found that when antimony is dropped into molten aluminum, it falls to the bottom and melts. No combination takes place until they are

<sup>1</sup> For an explanation of cooling curves, freezing-point curves, how they are obtained, etc., see Mathews: *J. Franklin Inst.*, Jan. and Feb., 1902, or *Eng. Min. J.*, Dec. 1901.

<sup>2</sup> *J. Soc. Chem. Ind.*, June, 1892.

stirred, when part of them unite and form an alloy which immediately solidifies on account of its high melting-point. The remainder stays molten because its melting-point is comparatively low. The solidified alloy has the composition 81.6 per cent. antimony, 18.4 per cent. aluminum.  $\text{SbAl}$  is a gray mass with an iridescent luster. Its melting-point is above  $1000^{\circ}\text{C}$ . which is most remarkable, considering that the melting-points of its ingredients are  $625^{\circ}$  and  $426^{\circ}$ , respectively (the melting-points should be  $655^{\circ}$  and  $632^{\circ}$ ). The alloys low in aluminum look like antimony, while those low in antimony are somewhat spongy. They all slowly disintegrate in the air and disengage hydrogen in water.

Roche<sup>1</sup> confirms the existence of the alloy  $\text{AlSb}$  with its abnormally high melting-point, but he claims that aluminum containing less than 5 per cent. antimony is malleable and superior in hardness, tenacity, and elasticity to pure aluminum. As the percentage of antimony is increased, the hardness and tenacity diminish until at 10 per cent. antimony, the alloy crystallizes in brilliant laminae. The melting-point and ease with which moist air attacks the alloy, increase up to 81.6 per cent. antimony, which in moist air or water crumbles to a black powder.

Richards says "The only useful alloy claimed by Roche is the one with less than 5 per cent. antimony. This, it is true, can be made apparently quite homogeneous, casts and rolls perfectly, and is apparently superior in many ways to pure aluminum, as remarked by Roche. But after a few months' standing it will be found that the alloy has disintegrated to such an extent as to be worthless, a point which has probably been discovered by this time." Our own experience has been the same as that of Richards.

Dr. Gautier, in his paper on the fusibility of metallic alloys,<sup>2</sup> points out that the curve of fusibility of these alloys is remarkable since nearly all its points correspond to temperatures higher than those of the fusion of the two metals. He says that the curve indicates the existence of the compound  $\text{SbAl}$ , whose fusing-point is slightly lower than that of pure copper.

On repeating this work with a recording pyrometer, we obtained a "complete freezing-point curve" of the series, which shows the lower breaks as well as the points of initial solidifica-

<sup>1</sup> *Mon. Sci.*, p. 265 (1893).

<sup>2</sup> *Bull. Soc. d'Enc.* [5], 1, Oct. (1896).



tion. Our curve differed from that of Dr. Gautier only at the point where the maximum occurs : whereas he placed it at about 85 per cent. antimony, 15 per cent. aluminum, we found it near 82 per cent. antimony, 18 per cent. aluminum. The compound  $\text{SbAl}$  ought to occur at 81.6 per cent. antimony. In the case of the alloys containing from 82–95 per cent. antimony we had great difficulty in taking pyrometric readings. The pipe-clay casing for the thermocouple was found to be quite pervious to part at least of the alloy, which by alloying with the platinum spoiled the record. On glazing the tube, this difficulty was only partially overcome, the method being far from safe. Glass was tried without success, for on cooling and solidifying, great strains are set up in the alloy and the glass was shattered. We were content to leave this part of the curve incomplete for the time being, because our microscopic examination was sufficient to fill in the missing parts. On a microscopic examination, these alloys fall into two groups :

1. 0 to 81.6 per cent. antimony, in which increasing amounts of the compound  $\text{SbAl}$  crystallize out in a groundmass of aluminum, or aluminum containing some antimony in solid solution, and having the same structure as pure aluminum.

2. 81.6 to 100 per cent. antimony, in which we pass from the compound  $\text{SbAl}$ , through a series of alloys composed of crystals of the compound in an increasing groundmass till we reach pure antimony. The groundmass of this group could not be resolved into two constituents and probably consists of antimony containing some aluminum (in the form of  $\text{AlSb}$ ) in solid solution for it melts  $2^\circ$  lower than pure antimony ;<sup>1</sup> that is, in the first series we have mixtures of aluminum and the compound  $\text{SbAl}$ , but no free antimony ; in the second we are dealing with alloys made up of aluminum antimonide and antimony, but no free aluminum. The series is remarkable in many ways. When the antimony reaches about 60 per cent., the alloys rapidly disintegrate in air into a fine powder. Gautier points out that this is due to oxidation, for if the alloy be weighed before and after disintegration it will be found to have gained weight, and if the fresh alloy be sealed *in vacuo* no change takes place. When the antimony in the alloy is between 50 and 85 per cent. a great expansion takes place during solidification, and part of the liquid interior of these alloys is squeezed out and solidifies as a button on top of the alloy.

<sup>1</sup> Gautier, *see ante*.

On examination, this part of the alloy which squeezed out was found to contain much less antimony than the original alloy. Edmond von Aubel<sup>1</sup> states that the compound  $\text{SbAl}$  melts at  $1078^{\circ}$ – $1080^{\circ}$  C., and has a specific gravity of 4.2176 at  $16^{\circ}/4^{\circ}$ , whereas the calculated specific gravity is 5.2246. Therefore the formation of this compound is accompanied by a relatively large increase in volume which manifests itself at the moment of solidification. The outer layer in the crucible or mold solidifies, expansion takes place, and the still liquid inner portions of the alloy are squeezed out in nodular masses. The nodules may in turn behave in the same way and a second part be squeezed out of their still liquid centers. It would naturally be supposed that the formation of these squeeze-buttons would alter the composition of the residual alloy so that analyses would have to be made of each. However, the largest buttons obtained were from alloys containing 60 and 75 per cent. antimony. When micro-sections of the buttons were made they corresponded closely with known alloys containing 50 and 60 per cent. antimony respectively, and the buttons constituted less than 10 per cent of the whole mass. By a simple calculation it is found that the residual alloys are probably not altered by more than 1 per cent. or 1.5 per cent. respectively, or at most by 2 per cent.

From the accompanying freezing-point curve (Fig. 5) it will be seen that a rise from aluminum (100 per cent.) to aluminum 67 per cent., antimony 33 per cent., is followed by a fall to antimony 37 per cent., after which the freezing-point rises uniformly to 81.6 per cent. antimony. The reason for the irregularity in the curve between antimony 33 per cent. and antimony 40 per cent., has not been found and the microscopic examination of these alloys offers no explanation. It may be that the difference is one of composition of the crystals, for it was noticed on etching, that the crystals in the 33 per cent. alloy were more easily attacked than those before or after it. It must be remembered in this connection that although the crystals consist primarily of the compound  $\text{SbAl}$  yet that need not be the sole constituent. Crystals isolated from series of alloys, though identical in form, are usually not definite in composition.

In the accompanying microphotographs examined in connection with the freezing-point curve it will be seen how the

<sup>1</sup> *Compt. rend.*, 132, 1266–7 (1901).



Fig. 6.

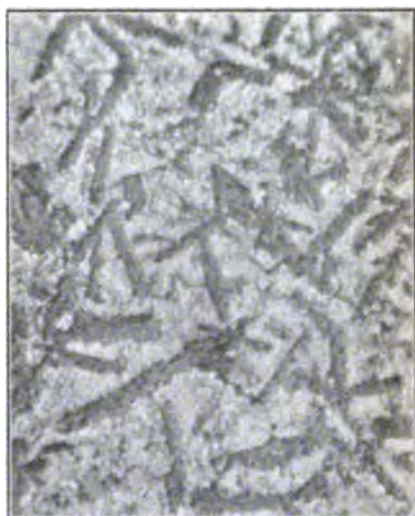


Fig 7.



Fig. 8.



Fig. 9.



crystals of  $\text{SbAl}$  increase toward the alloy whose freezing-point constitutes the summit of the curve. In those containing crystals plus aluminum, the groundmass decreases from aluminum 100 per cent. to aluminum 18.4 per cent., when it disappears; in those alloys which consist of crystals plus antimony, the groundmass decreases from antimony 100 per cent. to antimony 81.6 per cent. At the percentage corresponding to the summit in the freezing-point curve we should have a perfectly homogeneous mass consisting of pure crystals of the compound  $\text{SbAl}$ . Our figure, antimony 82 per cent., aluminum 18 per cent., shows nearly this condition. These are the two most reliable evidences of an intermetallic compound; *vis.*, a summit in the freezing-point curve which is afforded by an alloy which solidifies as a whole to a homogeneous mass at a single definite temperature. Alloys on either side of the summit consist of crystals of the compound decreasing in amount according to the distance they occur from the alloy of formula percentage, and disappearing entirely when the branch of the freezing curve in which the summit occurs disappears.

Fig. 6 shows an alloy containing 5 per cent. antimony, 95 per cent. aluminum, magnified 33 diameters and obliquely illuminated. Dark crystals of more or less pure  $\text{SbAl}$ , lath-like in shape, are seen in a granular groundmass consisting of aluminum or aluminum containing some antimony in solid solution.

Fig. 7 shows the alloy, 25 per cent. antimony, 75 per cent. aluminum. Similar to the above, but the crystals have increased in amount and size (33 diameters oblique).

Fig. 8 shows the alloy, 40 per cent. antimony, 60 per cent. aluminum. The dark crystals have become much larger and show a tendency toward parallel growth, thus forming large composite crystals. The groundmass is granular as before (33 diameters oblique).

Figs. 9 and 10 show, respectively, the alloy 60 per cent. antimony, 40 per cent. aluminum, and the squeeze-button resulting during the cooling of the original alloy. These and all the other alloys of the series are vertically illuminated. In these two, the compound appears bright and the groundmass of aluminum dark. The groundmass is decreasing rapidly and the crystals are beginning to interfere with each other, forming large masses of the

compound. In the crystals of the squeeze-button we see a number of skeleton triangles.

Fig. 11 is practically pure SbAl plus a little antimony which appears bright.

Fig. 12 shows 90 per cent. antimony, 10 per cent. aluminum,  $\times 33$  diameters. It is very friable and difficult to polish, and it is almost impossible to get rid of small pittings in the surface. Small crystals of SbAl are seen in a bright groundmass of antimony.

Fig. 13 shows 95 per cent. antimony, 5 per cent. aluminum, unetched. The crystals are much smaller and more regular than those of a 3 per cent. aluminum alloy but not so minute as those of a 10 per cent. aluminum alloy. Thus in passing from the compound SbAl to pure antimony, we find first the compound breaking up into very minute crystals, while, as the temperature of initial solidification decreases, we find the crystals increasing in size, but of course decreasing in number. This is just the reverse of what happens in the alloys on the aluminum side of the summit. So far we have found no solvent suitable for isolating the crystals. All those tried attack the crystals and even water decomposes them slowly. When a solvent is found, the crystals from the region of the irregularity in the freezing-point curve will be analyzed and their compositions compared. The etching of the alloys between 40 and 60 per cent. antimony generates considerable heat; in some cases this was sufficient to soften the cementing material used to fix the alloy upon glass for photographic purposes.

*Aluminum and Copper.*—In Gautier's curve of the melting-points of these alloys, we find maxima at about 50 and 88 per cent. copper, and minima at 33 per cent., 54 per cent., and about 92 per cent. Definite compounds certainly occur at the maxima, namely  $\text{Al}_3\text{Cu}$ , containing 48.4 per cent. copper, and  $\text{AlCu}$ , containing 87.6 per cent. copper. The fall in melting-point at 7.5 per cent. aluminum seems to indicate combination at this point,  $\text{AlCu}_2 = \text{AlCu} + \text{Cu}$ . Le Chatelier<sup>1</sup> has detected our compounds, viz.,  $\text{AlCu}_2$ , and probably  $\text{Al}_3\text{Cu}$ ,  $\text{AlCu}$  and  $\text{Al}_2\text{Cu}$ . He prepared the series of alloys by placing molten aluminum on molten copper and allowed the two to alloy at the junction and to

<sup>1</sup> *The Metallgraphist*, Jan., 1901.



Fig. 10.



Fig. 11.

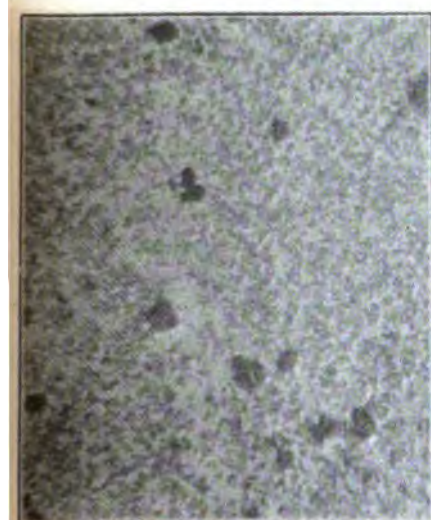


Fig. 12.

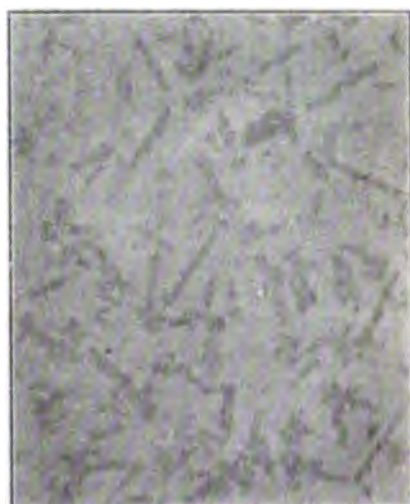


Fig. 13.





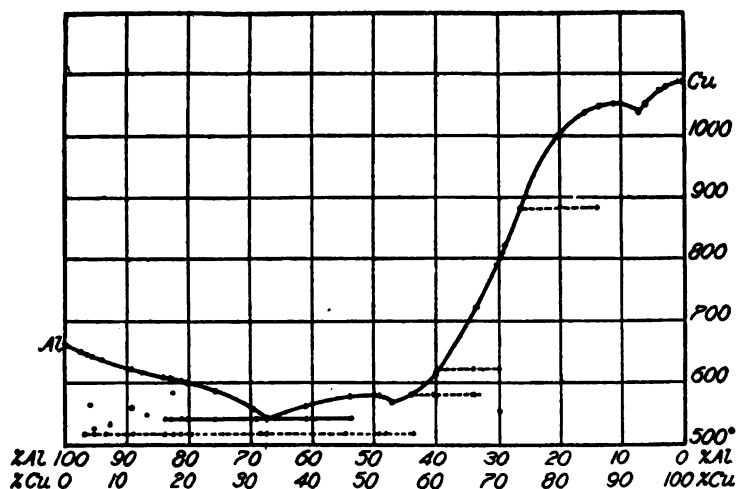


Fig. 14.

diffuse, thus obtaining the whole series of alloys between pure aluminum and pure copper. In connection with the drop in melting-point of the alloy at 56 per cent. we noticed also a corresponding irregularity of the specific gravity as compared with those alloys which precede and follow it. There is one well-marked eutectic (Fig. 14) melting at  $535^{\circ}$  and extending from about 10 per cent. copper to 48 per cent. copper. Between 0 and 10 per cent. copper we got a great number of minor points below the initial freezing-point, the meaning of which we have not determined. That the eutectic does not extend beyond 10 per cent. copper is due to the fact that aluminum can hold a considerable amount of copper in solid solution, which copper imparts certain advantageous properties to the aluminum. Beyond 50 per cent. copper the curve becomes very complicated, and we find three rows of subsidiary points indicated in the cooling curves. Their meaning will be revealed on microscopic examination if eutectics, or by a series of quenchings if changes in the solid.

At 88 per cent. we find a summit, corresponding to  $\text{AlCu}_2$ , and between this point and pure copper, no lower points on the cooling curves were observed. Yet the 93 per cent. alloy solidifies at a much lower temperature than either  $\text{AlCu}_2$  or pure copper. If, as LeVerrier surmises, there is a compound at 93 per cent. (or rather at 92.5 per cent. copper), then the alloys between this

and  $\text{AlCu}_3$  are solid solutions of one compound in the other, and those between 92.5 and 100 per cent. copper are solid solutions of  $\text{AlCu}_3$  in copper. We have only commenced work upon the micro-structure of these alloys. We hope ultimately to explain all the points in this curve which, as yet, are not understood. The long line of horizontal points below the eutectic line is as yet unexplained. As a basis for further study, we shall consider that all the alloys of aluminum and copper belong to three groups as shown by our curve: (1) From 0 to 48.4 per cent. copper, the alloys consist of aluminum and  $\text{Al}_2\text{Cu}_3$ ; (2) from 48.4 to 87.6 per cent. copper the alloys consist of the compounds  $\text{Al}_2\text{Cu}_3$  and  $\text{AlCu}_3$ ; alloys within this range contain neither free aluminum nor free copper; (3) from 87.6 to 100 per cent. copper, the alloys consist of  $\text{AlCu}_3$  and pure copper. These three pairs of constituents mixed or dissolved in various proportions probably compose all the possible alloys. The other compounds mentioned by LeChatelier seem to give no indications of their existence so far as pyrometric evidence is concerned.

METALLURGICAL LABORATORY OF THE  
ROYAL COLLEGE OF SCIENCE AND  
SCHOOL OF MINES,  
LONDON.

[CONTRIBUTIONS FROM THE HAVEMEYER LABORATORIES OF COLUMBIA UNIVERSITY, No. 48.]

## ON THE TEMPERATURE REACTION OF OILS WITH SULPHURIC ACID—MAUMENÉ'S TEST.<sup>1</sup>

BY H. C. SHERMAN, J. L. DANZIGER AND L. KOHNSTAMM.

Received October 26, 1901.

MAUMENÉ in 1852<sup>1</sup> showed that the rise of temperature on mixing with strong sulphuric acid is considerably greater with drying than with non-drying oils and that the difference may be of practical value in testing olive oil for the presence of poppy or other seed oils with which it may be adulterated. This method has generally been known as the Maumené test. As originally described and generally carried out, it consists in adding to 50 grams of the oil in a beaker, 10 cc. of strong sulphuric acid (according to Maumené, 66° Bé.), stirring with a thermometer, and observing the rise in temperature. Obviously it is essential that the test be always carried out under similar

<sup>1</sup> Read at the meeting of the New York Section of the American Chemical Society, June 7, 1901.

<sup>2</sup> *Compt. rend.*, 35, 572.

conditions and that the oil and acid have the same initial temperature, and it is desirable that the beaker in which the test is made be so surrounded as to minimize the loss of heat by radiation.

Various workers<sup>1</sup> have altered the quantities used by Maumené or employed more elaborate forms of apparatus for carrying out the test but none of these modifications seem to have come into very general use, perhaps because the extreme simplicity of the original method counts so strongly in its favor.

In general those oils which absorb more iodine will yield more heat on treatment with sulphuric acid, and since the iodine absorption can be quite accurately measured by the Hübl method there has been a tendency to regard the Maumené test as being of secondary importance in the examination of ordinary oils and of use mainly as a rough substitute for the Hübl method or as a preliminary "sorting test." Lewkowitsch does not include it among the "quantitative reactions." In many cases it is doubtless true that the information to be obtained by the Maumené test is given more accurately by the Hübl method, but the former possesses the great practical advantages of being much simpler and more rapid, of requiring no standard solutions or special reagents and only such apparatus as is always at hand. Hence if it could be made as accurate as the Hübl method it might often replace the latter with considerable saving of time and trouble. Moreover there are cases in which these methods do not give parallel results, and in which after the halogen absorption has been determined additional information may still be obtained from the Maumené test.

The errors affecting the Maumené test we believe to arise mainly from three sources :

(1) The secondary reactions which occur when the heat generated is considerable ; (2) the uncertainties involved in diluting the sample with some other oil to prevent too violent a reaction ; (3) variations in the intensity of the reaction caused either by differences in the strength of acid used or in the conditions affecting the radiation of heat.

The chief object of the work here described is to throw some

<sup>1</sup> Wiley : Bulletin 13, Division of Chemistry, U. S. Department of Agriculture, p. 443 ; and "Principles and Practice of Agricultural Analysis," Vol. III, p. 357. Jean : *J. Pharm. Chim.*, [5], 20, 337, (1889). Blasdale : *J. Am. Chem. Soc.*, 17, 935 (1895). Richmond : *Analyst*, 20, 58 (1895).

light upon these sources of error, and to ascertain if they can be minimized without sacrificing the simplicity of the original method.

In all cases we have used the proportions originally suggested, 50 grams of oil and 10 cc. of acid. To reduce the radiation of heat the beaker in which the test was made was either packed with asbestos in a larger beaker, or one of the smaller of a nest of beakers was used, the rest of the nest with the straw packing intact serving quite as well as the asbestos. The acid was added from a pipette of which the tip was drawn down so that the delivery of the 10 cc. occupied about fifty seconds. The mixture was thoroughly stirred with the thermometer until the maximum temperature was reached.

All of our results are stated as "specific temperature reaction" according to the suggestion of Thomson and Ballantyne;<sup>1</sup> that is, instead of giving simply the observed rise in temperature (which is largely affected by the strength of the acid and other conditions) this rise is multiplied by 100 and divided by the rise observed when 50 grams of water are treated with 10 cc. of the same acid under the same conditions.

In order to have a satisfactory basis for this calculation it is, of course, necessary that the 50 grams of water used shall completely cover the bulb of the thermometer. This limits the size of the beaker which can be used, and hence also the amount of frothing which may take place without loss of the determination. A deep narrow beaker or large test-tube has sometimes been used, but if the reaction is allowed to become so violent as to cause much frothing and evolution of volatile products, it is evident that heat will be lost. It thus becomes important in testing any but the non-drying oils that some means be taken to regulate the reaction.

This is accomplished by mixing the sample with a known proportion of some comparatively inactive oil. Maumené,<sup>2</sup> Bishop,<sup>3</sup> Ellis,<sup>4</sup> Jenkins,<sup>5</sup> and Gill<sup>6</sup> have used mineral oil for this purpose. Thomson and Ballantyne<sup>7</sup> used olive oil and Allen<sup>8</sup> suggests the use of olive or lard oil as a diluent.

<sup>1</sup> *J. Soc. Chem. Ind.*, 10, 233 (1891).

<sup>2</sup> Original publication by Imperial Academy, Rheims abs. by Ellis: *J. Soc. Chem. Ind.*, 5, 361 (1886).

<sup>3</sup> *J. Pharm. Chim.*, [5], 20, 302 (1889).

<sup>4</sup> *J. Soc. Chem. Ind.*, 8, 150, 361 (1886).

<sup>5</sup> *Ibid.*, 16, 194 (1897).

<sup>6</sup> "Handbook of Oil Analysis," p. 47, (1900).

<sup>7</sup> *J. Soc. Chem. Ind.*, 10, 234, (1891).

<sup>8</sup> "Commercial Organic Analysis," Vol. II, Part I, (3rd Edition) p. 79.

### INFLUENCE OF DILUENTS.

Mineral oil being cheaper and giving less heat with sulphuric acid than lard or olive oil, is the diluent most often used. Generally the sample and diluent are mixed in equal proportions, and the rise shown by 50 grams of the mixture is taken to be the mean between the rise given by 50 grams of diluent (which has been previously determined), and that which would be given by 50 grams of the sample.

This method assumes that the specific heat of the diluent is the same as that of the sample. As the different hydrocarbons which may occur in petroleum differ considerably in this respect, and some of them have specific heats much lower than those of the fatty oils, this assumption can hardly be regarded as free from error. The oils used in our own experiments, however, differed so little in their specific heats<sup>1</sup> that any discrepancy which may have arisen from this cause seemed negligible as compared with the other and greater uncertainties which the method involved; for it was found that whenever the reaction was moderated by the addition of mineral oil the result calculated from the mixture was much higher than that obtained by treating the same oil directly with the same acid.

Thus using an acid which gave with water a rise of 43°, we obtained the results shown in Table I in which the first column gives the values obtained by treating 50 grams of the sample directly with the acid, and the second column those calculated from the rise shown by a mixture of 25 grams of sample, and 25 grams of mineral oil. To facilitate the stirring of the mixture a thin oil (sp. gr. 0.817) was selected. This mineral oil alone gave with the acid a rise of 4°.

TABLE I.—EFFECT OF DILUTION WITH PETROLEUM UPON TEMPERATURE REACTION.

Oil tested.	Specific temperature reaction.	
	Direct treatment of oil with acid.	Oil diluted with petroleum as described above.
Lard oil.....	101	126
Olive oil.....	103	138
Almond oil.....	114	154
Sesame oil.....	158	200
Cottonseed oil.....	167	200
Peanut oil.....	176	194

<sup>1</sup> Approximate determinations of the specific heats of some of the samples gave the following values: olive oil, 0.493; lard oil, 0.50; raw linseed oil, 0.474; menhaden oil, 0.474; the mineral oil used as diluent, 0.50. We hope to extend these determinations later.

A few experiments were made in which olive oil, chloroform or carbon tetrachloride was used as the diluent, allowance being made for the low specific heats of the latter solvents. Although the discrepancies were not so great as with the petroleum the results obtained were somewhat too high. Olive oil, besides being liable to change from exposure, gives of itself sufficient rise with sulphuric acid so that only a small proportion of drying oil can be tested with it and any errors are multiplied in the calculation. The same is true of lard oil which seems to be even more liable to variation. With chloroform or carbon tetrachloride the proportion of drying oil to diluent must be small on account of the low boiling-point of the latter. By the use of a sufficiently large and constant proportion of a suitable solvent such as carbon tetrachloride, with very accurate thermometric measurements, and special precautions to prevent loss of heat, the reaction might be put upon a true calorimetric basis.<sup>1</sup> Such a method, however, would probably be too complicated to take the place now occupied by the Maumené test, and it seemed to us that a simpler and more satisfactory method would be to use a somewhat diluted acid instead of diluting the oil.

#### INFLUENCE OF THE STRENGTH OF ACID USED.

Thomson and Ballantyne<sup>2</sup> found that when the results were calculated as "specific temperature reaction" as above described, there was no apparent difference between those obtained with acids of different strengths, the acids used in their experiments being between 95 and 99 per cent. Working with somewhat weaker acids (89 to 95 per cent) we find a distinct difference according to the strength of the acid, the more concentrated giving a higher result although in each case the rise is referred to that given by water with the same acid. It is evident that the extent of the rise will be determined not only by the strength of the acid but to some extent also by the method of manipulation and the precautions taken to avoid radiation of heat. It seems better, therefore, to state the rise of temperature which an acid gives on mixing with water rather than its percentage strength. The acids are thus designated in Table II below which shows the specific temperature reactions of a number of oils with acids of different strengths.

<sup>1</sup> This has been undertaken by Mitchell (*Analyst*, 26, 169 (1901)), whose paper has appeared since the above was read.

<sup>2</sup> *Loc. cit.*

TABLE II.—EFFECT OF STRENGTH OF ACID ON SPECIFIC TEMPERATURE REACTION.

Sample.	Specific temperature reaction with acid which gave with water a rise of			
	33.3°.	37°.	40°.	43°.
Olive oil.....	90	96	100	103
Almond oil.....	95	100	108	114
Castor oil.....	84	88	89	94
Lard oil, I.....	81	89	92	95
Lard oil, II.....	88	95	99	101
Arachis (peanut).....	161	..	..	176
Rape oil.....	144	..	160	..
Cottonseed oil.....	152	..	..	167
Sesame oil.....	143	..	..	158
Sperm oil.....	102	106	..	111
Resin oil.....	72	..	..	72

It will be seen that with all of the fatty oils examined the specific temperature reaction became higher as the strength of the acid was increased from 89 to 95 per cent. The differences seem to be as great with the non-drying as with the semi-drying oils. The sample of resin oil showed no difference.

#### SPECIFIC TEMPERATURE REACTION WITH DILUTED ACID.

It is evident that the use of an acid of 89 to 90 per cent., giving with water a rise of 33° to 34°, will usually yield results somewhat lower than would be obtained with acid of 95 to 99 per cent. as used by Thomson and Ballantyne. It is believed, however, that the figures obtained with the weaker acid will be more uniform since the temperature rises more steadily and there is less frothing and evolution of sulphur dioxide than when the stronger acid is used. The secondary reactions and the errors arising from inaccuracy in reading a rapidly changing temperature are thus considerably reduced. The great advantage, however, is that the simple method heretofore used in testing the non-drying oils can, with the diluted acid, be applied to all oils alike and the results obtained with the drying and non-drying oils become comparable with each other. Table III shows the results obtained with 89 per cent. acid upon several samples of oils of which the specific gravities, Hübl figures, and acidity are also given.

TABLE III.—SPECIFIC TEMPERATURE REACTIONS OF OILS WITH SULPHURIC ACID.

No.	Description of oil.	Specific gravity. 15.5° 15.5°	Hübl figure.	Free acid as oleic. Per cent.	Specific temperature reaction.
1.	Linseed (raw), 1900.....	0.934	182.4	4.30	300
2.	Linseed (raw), 1898.....	0.938	175.9	1.22	298
3.	Poppyseed, age unknown..	0.926	129.6	2.66	212
4.	Peanut (arachis), 1899 ....	0.917	105.9	0.16	161
5.	Maize, 1900.....	0.924	120.3	3.32	158
6.	Maize, 1898.....	0.926	120.7	2.56	168
7.	Rape, age unknown.....	0.920	108.6	0.68	155
8.	Rape, 1901.....	0.920	107.4	0.82	144
9.	Cottonseed I, 1900.....	0.920	102.5	0.20	147
10.	Cottonseed II, 1900.....	0.921	106.4	0.32	157
11.	Cottonseed III, 1900.....	0.923	105.5	0.08	152
12.	Cottonseed, old.....	0.926	103.0	0.44	197
13.	Cottonseed, very old.....	0.941	93.7	2.03	245
14.	Sesame, 1899.....	0.924	105.3	1.65	143
15.	Almond, 1898.....	0.919	98.1	5.13	95
16.	Olive, 1899.....	0.917	85.1	2.51	90
17.	Castor, 1898.....	0.964	86.9	2.18	84
18.	Menhaden, refined.....	0.935	....	0.36	309
19.	Menhaden, crude, 1899....	0.934	....	1.92	356
20.	Codliver, 1901.....	0.926	149.6	....	280
21.	Codliver, 1900.....	0.927	165.6	0.56	259
22.	Seal, 1901.....	0.926	140.6	....	255
23.	Lard oil, 1900.....	0.917	74.3	0.74	81
24.	Lard oil, 1899.....	0.919	72.5	1.25	88
25.	Lard oil, 1897.....	0.924	69.3	2.34	122
26.	Sperm oil, age unknown...	0.886	78.7	0.78	102
27.	Resin oil, age unknown...	0.989	76.9	14.40	72

The samples marked "1900" were obtained directly from the makers and were undoubtedly pure and reasonably fresh. The other samples were purchased from responsible dealers in the years indicated, and are believed to be pure. Numbers 12, 13, and 25 are examples of oils exhibiting some abnormality which is much more strikingly shown by the temperature reaction than by the other determinations. As each of these samples is some years old and has a high specific gravity it is probable that they had become somewhat oxidized by exposure. These three samples are omitted from the averages given below.

## COMPARISON OF ABOVE RESULTS WITH THOSE OF THOMSON AND BALLANTYNE.

Table IV shows in parallel columns the averages of the deter-



minations of specific temperature reaction published by Thomson and Ballantyne,<sup>1</sup> who have done most toward putting the test upon a satisfactory basis, and those obtained by us as described above and shown in detail in Table III.

TABLE IV.—COMPARISON OF AVERAGE RESULTS—SPECIFIC TEMPERATURE REACTION.

Description of oil.	Thomson and Ballantyne.		Table III above.	
	No. of samples examined.	Average figure.	No of samples examined.	Average figure.
Linseed (raw) .....	4	315	2	299
Poppyseed.....	..	...	1	212
Maize .....	..	...	2	163
Cottonseed .....	3	167	3	152
Rape.....	5	133	2	150
Peanut (arachis).....	2	121	1	161
Sesame.....	..	...	1	143
Almond .....	..	...	1	95
Olive.....	11	92	1	90
Castor.....	2	91	1	84
Menhaden.....	1	306	2	333
Codliver.....	3	254	2	270
Seal.....	4	222	1	255
Whale .....	1	157	.	...
Lard oil.....	..	...	2	85
Sperm oil .....	1	100	1	102
Arctic sperm.....	1	93	.	...
Rosin oil .....	..	...	1	72

With most of the vegetable oils the results obtained by us with the diluted acid are slightly lower than those reported by Thomson and Ballantyne, while with the few animal oils compared our results are a little the higher. In general the agreement between the two sets of results is sufficiently close to indicate that the adoption of the modification here used involves no radical departure from what has heretofore been considered the best practice.

## A NOTE ON THE DETERMINATION OF MOLYBDENUM IN STEEL.<sup>2</sup>

BY GEORGE AUCHY.

Received January 23, 1902.

UP to recently the analyst has not often been called upon to determine molybdenum in steel, but in the future this determination will be frequently made. To steel works chemists

<sup>1</sup> *Loc. cit.*

<sup>2</sup> Read at the meeting of the Philadelphia Section of the American Chemical Society, January 16, 1902.

accustomed to determining phosphorus indirectly from the volumetric estimation of the molybdic acid in the yellow precipitate by zinc and permanganate, this would seem to be the easiest and simplest way also of determining molybdenum in steel; first, of course, separating the molybdenum from the iron by ammonia or soda. The point to be settled is: Can the molybdenum be completely separated from the iron by one precipitation with ammonia or caustic soda?

It will be found upon trial that the use of ammonia in only moderate excess, at least, is entirely out of the question. But the following results indicate that caustic soda answers sufficiently well for practical purposes, though not perfectly. Perfect separations by this reagent were, however, obtained by Ibbottsen and Brearly.<sup>1</sup> In these tests the molybdenum was determined gravimetrically in an aliquot part of the filtrate.

	Per cent.	Per cent.	Per cent.	Per cent.
Molybdenum present.....	5.23	5.23	5.23	5.23
Molybdenum found .....	5.26	5.14	5.18	5.22

In the following, the molybdenum in the filtrate was determined volumetrically—zinc and permanganate.

No.	Molybdenum present. Per cent.	Molybdenum found. Per cent.
1 .....	5.23	5.14
2 .....	5.23	5.14
3 .....	1.05	1.07
4 .....	2.10	2.11

The writer proceeds as follows: Not more than 1.308 grams of steel are treated with a large excess of strong nitric acid and a little potassium chlorate (if chromium is also present, as is usually the case); the nitric acid is evaporated off, boiled with strong hydrochloric acid, and evaporated to dryness to separate silica; again taken up with strong hydrochloric acid and evaporated to first appearance of scum. Then 5 cc. strong hydrochloric acid, diluted to 20 cc. with water, are added and heated to effect complete solution. The volume of the liquid is made up to 50 cc. and poured, little by little, with shaking, into 20 grams caustic soda dissolved in 100 cc. water in a 12-ounce Erlenmeyer flask, provided with a file mark at 300 cc. The liquid is diluted to this mark and mixed by shaking around in the flask, allowed to settle, and filtered into a 250 cc. measuring flask, until it reaches the mark. Then trans-

<sup>1</sup> *Chem. News*, 82, 2137.

ferred to a beaker, acidified with sulphuric acid, boiled down to less than 100 cc., and finished as in phosphorus determinations, by reducing with zinc, and titrating with permanganate.

The blank or dummy test is a highly important one. It must be done on a molybdenum-free steel in exactly the same way as the test: the same amount of hydrochloric acid and the same amount of chromium. Both the hydrochloric acid and the chromium affect the dummy, the former very greatly, and the latter slightly.

	Permanganate. cc.
Dummy test, without hydrochloric acid.....	0.6
Dummy test, with hydrochloric acid.....	1.2

Below are results obtained by use of the latter dummy result (chromium not added) in steels containing same amount of chromium as molybdenum.

No.	Molybdenum present. Per cent.	Molybdenum found. Per cent.
1 .....	1.05	1.12
2 .....	2.61	2.65
3 .....	5.23	5.35

Although the most of the chromium is precipitated with the iron, it would seem from these results that enough passes into solution to slightly affect the end-point of titration. Hence the necessity for its presence in the dummy test.

In the gravimetric method the first lead molybdate precipitate is always contaminated with a little chromate.

LABORATORY OF HENRY DISTON & SONS' STEEL WORKS,  
PHILADELPHIA.

## PRELIMINARY NOTE ON A NEW SEPARATION OF THORIUM.

BY FLOYD J. METZGER.

Received January 6, 1908.

**I**N an investigation still in progress, attention has been particularly directed to the use of the weaker organic acids for the separation of thorium from cerium, lanthanum, and didymium, and it is in this field that it is desired to announce some preliminary results.

It is found that from a 40 per cent. alcoholic solution, thorium is precipitated quantitatively on the addition of fumaric acid, while no change is produced by that reagent in cold solutions of cerium, lanthanum, or didymium.

The experiments already made show that a good quantitative separation of thorium from these elements can be based upon this reaction. When thorium is precipitated in this manner in the presence of either cerium, lanthanum, or didymium, traces of the latter elements are carried down, but may be removed by a single reprecipitation. It is intended to compare this method with those at present in use for the analysis of monazite.

A number of other weak organic acids are being investigated along the same lines, and several of these show interesting results.

QUANTITATIVE CHEMICAL LABORATORY,  
COLUMBIA UNIVERSITY.

---

#### NOTE.

*Reinsch's Test for Arsenic.*—To obtain a black deposit upon a piece of copper is a comparatively easy matter; to prove that this deposit is due to the presence of arsenic is perhaps more difficult. In place of the usual glass tube, Sheridan Delépine<sup>1</sup> recommends a "thimble-shaped copper cone" half an inch high, inserted through a hole in a thin iron plate, the sublimate of arsenious oxide being formed on a microscope cover glass. The following simplified form of the above arrangement I have found extremely convenient for the detection of very minute quantities of arsenic.

In the center of a piece of sheet copper an inch or so square, a small depression is punched, an eighth of an inch deep and of about the same diameter. The arsenic is deposited from solution on a little piece of copper a few millimeters in area. After being washed and dried, the little piece of blackened copper is placed in the depression in the sheet metal. A microscope cover glass, having a drop of water on its upper surface, is now placed over the miniature copper crucible, and the latter is then gently heated over a very small flame. When examined under a high power of the microscope, the crystals of arsenious oxide may sometimes be seen even when no sublimate is visible to the naked eye. Careful attention to the illumination is, of course, necessary.

UNIVERSITY OF MANITOBA,  
WINNIPEG.

EDGAR B. KENRICK.

<sup>1</sup> Abstract in *J. Soc. Chem. Ind.*, March, 1901.

## NEW BOOKS.

**ON THE COMPOSITION OF DUTCH BUTTER.** BY DR. J. J. L. VAN RYN. London : Ballière, Tindall and Co. 1902. 55 pp.

Samples of pure butter from Holland having been declared by English chemists to be mixtures of butter and margarine, the Netherlands government directed Dr. van Ryn to make an investigation of the variation in chemical composition of Dutch butters known to be genuine, in order to ascertain the cause of the abnormal composition.

In the first portion of his treatise, the author discusses the characteristics of pure butter, especially with reference to the percentage of volatile fatty acids as represented by the Reichert-Wollny number. He calls attention to the various factors influencing this number, such as advance of lactation, food, environment, etc., stating the views of various authorities.

The second portion of the paper gives the detailed results of his investigation. Samples of butter were obtained during the months of September, October, November, and December, from thirteen different herds, varying in size from 3 to 144 cows each, and from twelve different creameries. It was during the fall months that Dutch butters had been found abnormal. The author gives statements as to number, breed and age of cows, dates of calving, nature of soil, kind of food, and date of stabling. The tabulated analytical results are given under the heads of refraction, specific gravity, volatile acids (Reichert-Wollny), insoluble and soluble acids (Hehner), saponification number (Koehtstorfer), and iodine number (Hübl).

The volatile acid number was found to be the best factor to use in studying changes of composition. The following statements indicate the most important results reached :

1. Of 428 samples of pure butter examined, just one-half fell below 25 in respect to the volatile acid number, this figure being the lowest limit accepted in England for pure butter. Nearly 10 per cent. of the samples were below 22.

2. The amount of volatile fatty acids began to decrease in September, and reached its lowest point in October, after which it rose gradually, as indicated by the following monthly averages : September, 24.8 ; October, 23.7 ; November, 25.2 ; December, 26.6.

3. The author concludes that the abnormal chemical composition of Dutch butter during the autumn is largely due to the fact that the farmers leave their cows in pasture until late in the year, subjecting the animals to the combined adverse influences of poor food and inclement weather. When cows are stabled earlier and well fed, this abnormal composition is not observed.

L. L. VAN SLYKE.

**THE MANUFACTURE OF ALUM AND THE SULPHATES AND OTHER SALTS OF ALUMINA AND IRON.** BY LUCIEN GESCHWIND. New York: D. Van Nostrand Co. 1901. 8vo. Cloth. 387 pp. Illustrated. Price, \$5.00.

Since so little has been written concerning the technology of these subjects, this book is an important addition to this literature. The author has gathered much information about the chemical properties of iron, aluminum and their compounds, which makes this book valuable as a handbook by giving the chemist easy access to information without having to search through volumes to obtain it.

If, however, the author had given more attention to the processes of manufacturing, this book would have been very much more valuable. The methods of making alum, sulphate of alumina, and sulphates of iron from shale, have, in this country, only an historical interest. American manufacturers would not think of operating a sulphate of alumina works according to the methods, which, the author states, are carried on in France.

The book is divided into four parts; *viz.*, first, a theoretical study of iron, aluminum and their compounds; second, the manufacture of the sulphates of iron and aluminum; third, the uses of the sulphates of iron and aluminum; fourth, analysis of iron and aluminum.

A review is given of many of the different methods which have been employed and are now used to obtain aluminum, but the Hall process, which has made cheap aluminum possible, and which is the most important method used, is not even mentioned.

As indicated above, the methods mentioned for making aluminum sulphate are not up to date. The grinding of only 400 pounds of bauxite to 60 mesh per hour is quite insufficient. Stirring a mix by hand is too expensive, and the new method employed at the Noyen works is not the best that could be used. The American trade requires a sulphate of alumina containing 17.5 per cent.  $Al_2O_3$ , of which 1.5 per cent. is basic. Such a cake

can be far more readily ground than the one Geschwind described containing 16 per cent.  $\text{Al}_2\text{O}_3$ .

In the chapter describing the method of purifying aluminum sulphate, it is stated that the introduction of zinc sulphate is disadvantageous. On the contrary, it is very advantageous with animal-sized paper, and is specifically required by many paper-makers in this country. If the author had included American practice, this chapter would have been much more interesting.

The method described for making crystal alum is essentially the same as that used in this country. The figures which are given are of much interest to any alum-maker.

The method given for analyzing bauxite for alum purposes is open to criticism. It will give too high results. The method of attack used in analysis to determine the alumina available for alum-making, should as nearly as possible correspond to the reaction which takes place in the mix tank.

The chapter on the uses of the sulphates is very interesting and instructive. No one who is interested in these manufactures should be without this book.

Notwithstanding its omissions the book is of sufficient importance to make it very valuable to those engaged in these manufactures, and to the chemical student.

C. D. VREELAND.

VORLESUNGEN UEBER THEORETISCHE UND PHYSIKALISCHE CHEMIE. ERSTES HEFT—DIE CHEMISCHE DYNAMIK. BY J. H. VAN 'T HOFF. Second Edition. Braunschweig: F. Vieweg und Sohn. 1901. xi + 251 pp. Price, 6 M.

Hardly three years and a half have elapsed since the appearance of the first edition of this part of the "Lectures." Its rapid succession by a new edition—or rather, a reprint—bears eloquent testimony, if any had been needed, to the conspicuous merits of the work. In this part of the subject, dealing with chemical equilibrium and reaction speed, the author is particularly at home, for references to his own or his pupils' investigations appear in almost every section. Whether we consider the original arrangement of the material or the masterly handling of the details, the book must be declared eminently successful. The characteristics of the treatment are so familiar to those who possess the first edition, or the English translation by Dr. Lehfeldt, that they need not be described here. In the present edition the only change,

beyond merely verbal ones, which we have noticed, is the omission of about a page dealing with Mallard and Le Chatelier's theory of the speed of propagation of combustion in gases. It is unfortunate that the statements in regard to the work of Helier and of Pelabon (pp. 207 and 232) on false equilibria have not been modified in view of Bodenstein's conclusions published two and a half years ago. It appears, however, from the preface that the revision was completed before that time, so that recent work of importance had to remain unnoticed. Besides the work does not profess to be exhaustive and the selection made presents all the types most admirably.

ALEXANDER SMITH.

THE CHEMICAL ESSAYS OF CHARLES WILLIAM SCHEELLE. Translated from the transactions of the Academy of Sciences at Stockholm with additions. First published in English by J. Murray, 32 Fleet St., London, in 1786. With a sketch of the life of Karl Wilhelm Scheele, by John Geddes McIntosh. Reissued by Scott, Greenwood & Co., 19 Ludgate Hill, London, E. C. 1901. xxx + 294 pp. 8vo. Price, 6 shillings.

The first collection of the chemical essays published by Scheele in the Memoirs of the Royal Academy of Sciences, Stockholm, was issued at Dijon in 1785, and filled two small volumes; the translation from the Swedish and the German (for Scheele wrote and published in both languages) was made by Madame Picardet, and her manuscript was revised by the prominent chemist Guyton de Morveau. It is interesting to note that the lady afterwards became Madame de Morveau.

Then appeared the English edition of 1786 named in the title-page of the book under review; this was followed by a Latin edition by E. B. G. Hebenstreit (Leipzig, 1788-1789), and finally by a German edition edited by S. F. Hermbstädt, published at Berlin in 1793, and reissued in 1891. As Scheele died May 21, 1786, the only one of these collections published in his lifetime was the French edition of 1785.

None of these contain, however, one of Scheele's most important researches "On Air and Fire," in which he describes the discovery of oxygen; this appeared in German, at Upsala and Leipzig in 1777; an English translation (with notes by Richard Kirwan and Joseph Priestley) followed in 1780. Finally in 1892, A. E. Nordenskiöld published, at Stockholm, Scheele's "Nachgelassene Briefe und Aufzeichnungen," a sumptuous volume of 491 pages royal 8vo, illustrated with portraits and facsimiles.



Scheele's remarkable discoveries are well known, their chronological sequence is approximately as follows :

1770, tartaric acid ; 1771, hydrofluoric acid ; 1774, chlorine, oxygen, and barytes ; 1775, benzoic and arsenic acid ; 1776, uric acid ; 1777, sulphuretted hydrogen ; 1777, action of light on silver salts ; 1778, arsenite of copper, "Scheele's Green," molybdic acid ; 1779, composition of graphite ; 1780, sugar of milk, lactic acid, mucic acid ; 1781, composition of "scheelite," tungstic acid ; 1783, glycerin, prussic acid ; 1784-1785, citric, malic, oxalic and gallic acids.

And the poor apothecary, who accomplished all this in fifteen years, died before he was 44 years of age !

The reprint under review exactly reproduces the contents of the original edition, which does not contain a complete list of Scheele's papers ; the new work might have been made more valuable by including additional treatises, notably those on air and fire.

In arranging the chronological list of Scheele's discoveries, the reviewer assigns 1774 as the date for the isolation of oxygen, though he is aware that Scheele's biographer, Nordenskiöld, endeavors to prove that the gas was known to the Swedish chemist before 1773.

Scheele's essays are written, of course, in the language of the phlogistic theory, and this in some measure obscures their real meaning, when read by chemists of the present day. But by re-writing a paragraph or two in modern style, carefully avoiding later knowledge, it is interesting to note how clearly Scheele expressed himself.

The publishers of this reprint have done their part well, making a handsome volume ; the editor has supplied a rather scanty biography, without a bibliographical note or comment, omitting all reference to the facts mentioned in the volume by Nordenskiöld. The reprint would have been increased in value by the addition of a portrait of the Swede. The volume has an index.

HENRY CARRINGTON BOLTON.

ANNUAIRE POUR L'AN 1902, PUBLIE PAR LE BUREAU DES LONGITUDES.  
16mo. 700 pp. Paris. 1902. Price, 1 fr. 50 c.

This volume differs from its well-known predecessors in containing revised tables of coinages, the census of Europe made in 1900, articles on wireless telegraphy by Poincaré, on polyphase

currents by Cornu, on the decimal division of the quadrant by Guyon, and on the Mont Blanc observatory by Janssen. The tables of electrochemical equivalents are well done, and there are many tables on heat, sound, light, and electricity, which might be occasionally referred to, and which are in the main reliable. The first half of the book is devoted to the annual discussion of calendars and astronomical data. J. W. RICHARDS.

**THE DYEING OF COTTON FABRICS.** A Practical Handbook for the Dyer and Student. BY FRANKLIN BEECH. 44 illustrations. Price, \$3.00.

This is a practical handbook, very well adapted for the use of the dyer and the student. Two hundred and sixty-eight pages devoted to a description of this important industry cannot, of course, exhaust the subject, and Mr. Beech tells us in the preface that such was not his intention. Though brief, the book is sufficiently detailed for the so-called "practical man". The purely chemical side of the subject has received scant attention, as might be expected.

The processes described are modern but the addition of descriptions of some of the newer methods of bleaching is necessary in order to bring the subject down to date. In the chapters on the principles and the practices of dyeing, the author gives a large number of receipts for obtaining various shades. Probably many useful hints may be culled from these, though their value would have been considerably enhanced by the addition of information as to the makers of the various colors used. The chapters on dyeing, however, treat the subject very satisfactorily.

The book is lucidly written, well printed, well illustrated and well bound, and it has a good index. C. W. PARMELEE.

**MODERN CHEMISTRY. PART FIRST, THEORETICAL CHEMISTRY.** 126 pp. **PART SECOND, SYSTEMATIC CHEMISTRY.** 203 pp. BY WILLIAM RAMSAY, D.Sc. The Temple Cyclopaedic Primers. London: J. M. Dent & Co. 1900. Price, 1s each.

It is difficult to decide for what class of readers these books are intended. Persons unacquainted with chemistry would certainly have great difficulty in understanding them, while chemists would not naturally turn to a primer for information.

In these little volumes, an examination discloses, however, an adequate, though condensed, presentation of theoretical and systematic chemistry. Their size alone, justifies the use of the title

primer. While the compounds of carbon and the compounds of some of the less important elements receive but little attention, no theory, no formula, no fact has been omitted out of consideration for the youthful mind, that is supposed to be most in need of elementary instruction. The theory of ionization is freely used, adding to the freshness, which characterizes the systematic portion of the text. Descriptions of experiments, and illustrations, are seldom given, and are not needed by the class of readers to which these books are suited. Students who have already gained an acquaintance with the elements of chemistry, will find them helpful, but for beginners their fitness is questionable.

L. B. HALL.

INDUCTION COILS. BY H. S. NORRIE (Norman H. Schneider). Second edition. New York: Spon and Chamberlain. 1901. xvi+270 pp. 13×17 cm. Cloth. Price, \$1.00.

This book, which is a revised and enlarged edition, contains fairly detailed, practical directions for making and operating the various types of induction coils in common use. The important subject of contact breakers is treated in a special chapter. The volume contains additional chapters on spectrum analysis, currents *in vacuo*, batteries for running coils, Tesla and Hertz effects, Roentgen rays, and wireless telegraphy. The chapter on spectrum analysis is introduced into the book in a very artificial manner. It is very inadequate and not free from error. Thus on page 135 we read, for instance, "The spectrum of hydrogen gives two very bright lines of red and orange." The book gives evidence throughout, that it has been written for the amateur. Rules for doing certain things are laid down without indicating the underlying principles; and when a feeble attempt at scientific explanation is made, the author frequently clearly demonstrates that he does not himself possess a firm grasp of the principle involved. Thus, for example, on page 180 in explaining the polarization of a Leclanche cell is this statement, "a film of hydrogen, which is a poor conductor, forms over the negative plate, increasing the internal resistance of the cell and setting up local action." It is impossible to go into further details here; but it naturally follows, that because the author is not always clear in his own mind as to the underlying principles, his directions for doing things are not always the best.

The induction coil is an important piece of apparatus in the

chemical laboratory. Its use is steadily increasing. The chemist may at times find some helpful suggestions in the chapters on coils and their use contained in this book.

LOUIS KAHLENBERG.

LECTURES ON THE HISTORY OF THE DEVELOPMENT OF CHEMISTRY SINCE THE TIME OF LAVOISIER. BY DR. A. LADENBURG. Translated from the second German edition, by Leonard Dobbin. (With additions and corrections by the author.) Edinburgh: Published by the Alembic Club. William F. Clay, Edinburgh, Agent; Simpkin, Marshall, Hamilton, Kent, & Co., Ltd., London agents. 1900. 12mo. xvi + 373 pp.

Since the appearance at Leyden, in 1561, of the little 46-page 16mo. by Robert Duval, entitled "*De veritate et antiquitate artis chemicae*," commonly regarded as the first history of chemistry, this topic has been the subject of a score or more of volumes, differing greatly in scope and method of treatment. Duval's essay contains sentences and paragraphs from genuine and many fictitious writings by theologians, physicians, poets, and philosophers thought to be pertinent. This early attempt was followed about one hundred years later by the "*De ortu et progressu chemiae dissertatio*" of Olaus Borrichius, a curious example of the extravagant credulity of a learned man; but it was not until the very end of the eighteenth century that the history of chemistry was attacked in a serious way by the distinguished chemist J. F. Gmelin, who produced an unwieldy, badly arranged work in three volumes.

These were followed by the sketchy volumes of Thomas Thomson (London, 1830), the systematic work of Ludwig Franz Bley (Halle, 1834), and the comprehensive study of Ferdinand Hoefer (Paris, 1842, 2 vols.). Then appeared the erudite, exhaustive, four-volume "*Geschichte der Chemie*" of the scholar Hermann Kopp, which has proved an indispensable mine of information to nearly all its successors.

Two French historians have shown marked national bias; Béchamp's "*Lettres historiques*" (Paris, 1876) are dedicated to the memory of Lavoisier "unjustly outraged by the German chemists Kolbe, Liebig and Volhard;" and Jagnaux's "*Histoire*" (Paris, 1891, 2 vols.) is avowedly written to demonstrate the truth of the phrase used by another Frenchman: "Chemistry is a French Science."

Berthelot, the eminent chemist who also held a position in the

French Cabinet, gave to historians new and valuable material in his six quarto volumes on the ancient Greek alchemists, and the writers of the middle ages, but the most carefully written general history of recent date is that of Ernst von Meyer (Leipzig, 1889), and that of A. von Ladenburg, which is now under review in its English dress.

This is not a history of chemists and their labors but a philosophical study of the growth of the science since the period when Lavoisier placed it on a firm basis; the author magnifies the part played by Lavoisier, shows the origin of the false claim made for Wenzel, does justice to Richter who introduced the term stoichiometry, points out that the atomic weights of Dalton were rather arbitrarily ascertained, though he says nothing to belittle his genius.

The fact that the matter is presented in lecture form has its advantages, and assists the author in his attempt to follow the development of our present ideas from those that were formerly current; while written concisely, the student can pursue given topics more thoroughly by referring to the many treatises and articles named in foot-notes.

As thirty years elapsed between the first publication of the work in German and the appearance of this English translation, Dr. von Ladenburg has added another chapter, bringing the history down to date. In this he does justice to the labors of Gibbs, Ostwald, and van't Hoff in developing the physical aspect of chemistry, the ionization theory, and the advance made in electrochemistry. Dr. von Ladenburg's lectures are altogether the strongest writings on the development of the recent aspects of chemistry, and are recommended to readers seeking an adequate presentation of this subject.

The English translation is admirable; we notice, however, a few blemishes in proof-reading; *e. g.*, "Mon-atshefte," and 1771 for the date of Priestley's discovery of oxygen. The indexes to names of persons and to subjects are in distinct alphabets, an arrangement the advantages of which are not evident.

HENRY CARRINGTON BOLTON.

EXPERIMENTS ON LOSSES IN COOKING MEATS. BY H. S. GRINDLEY. Bulletin No. 102, U. S. Department of Agriculture, Office of Experiment Stations. Washington: Government Printing Office. 64 pages.

This pamphlet gives the results of investigations carried out in

the laboratories of the University of Illinois in the years 1898-1900, and is one of a series of similar publications sent out from the Office of Experiment Stations. Many of these publications have to do with the broad question of the practical nutrition of man and in this interesting bulletin the results of about twenty-five complete experiments on the losses resulting in cooking meats in different ways are detailed. The methods of analysis employed are also given when necessary, which adds to the value of the pamphlet for those engaged in similar researches.

J. H. LONG.

THE PRACTICAL METHODS OF ORGANIC CHEMISTRY. BY LUDWIG GATTERMANN, PH.D. Translated by WILLIAM B. SCHÖBER, PH.D. Authorized translation. The second American from the fourth German edition. New York: The Macmillan Co. 1901. xv + 359 pp.

This book is so well known in the original that the second English edition translated from the fourth German edition needs no special introduction. The work has served its purpose so admirably that it is already well known to all workers in the field of organic chemistry. The translation is excellent, and as was stated in the preface to the first English edition it "is intended for those students of chemistry who have not yet become sufficiently familiar with scientific German to be able to read it accurately without constant reference to a dictionary." In the present edition a number of new illustrations have been added and in many cases the laboratory directions have been improved. In that part of the book dealing with preparations, methods for the preparation of the following substances have been added: glycol, dimethylcyclohexanone, *s*-xyleneol, phenylhydroxylamine, nitrosobenzene, *p*-tolyl aldehyde (Gattermann-Koch synthesis), salicylaldehyde (Reimer and Tiemann's oxyaldehyde synthesis), cuprous chloride, the decomposition of inactive mandelic acid into its active constituents, and a zinc dust determination.

H. FAY.

LOGARITHMS OF NUMBERS AND CHEMICAL FACTORS. BY CHARLES R. SANGER. Publication Office of Harvard University, 1901.

This publication in the form of a large card, is essentially a fifth edition of the well-known table of Wolcott Gibbs. It is based on the table of atomic weights which was compiled by Richards in April, 1901, and covers thirty-seven elements. The logarithms are those which are required for the reduction of

ordinary analytical data, such as the calculation of K or  $K_2O$  from  $K_2PtCl_6$ , etc., and they are presented in very compact and convenient form. To chemists who are accustomed to compute from factors rather than from direct atomic weights this work is undoubtedly useful.

F. W. CLARKE.

AN INTRODUCTION TO CHEMICAL ANALYSIS, FOR STUDENTS OF MEDICINE, PHARMACY AND DENTISTRY. BY ELBERT W. ROCKWOOD, M.A., M.D., professor of chemistry and toxicology in the college of medicine; professor of chemistry and metallurgy in the college of dentistry; lecturer on toxicology in the college of pharmacy, of the University of Iowa. Illustrated. Philadelphia: P. Blakiston's Son & Co. 1901. Price, cloth, \$1.50 net.

This book first treats of the general plan of analysis and of apparatus and reagents, technical terms employed and explains general operations.

The author assumes that there has been some previous study of general chemistry or that this study is pursued at the same time. He does not refer to other works.

The book is divided in four sections: the first and second embrace qualitative and quantitative analysis respectively; the third, applied analysis, includes the sanitary examination of water, detection of poisons and blowpipe analysis; the fourth includes preparation and testing of reagents (in tabular form), tables of elements and atomic weights, and the metric system.

Under quantitative analysis there is a chapter on organic compounds comprising under each a short chemical characterization and methods of testing for purity.

Appended to each qualitative group are a number of questions calculated to aid the student in fixing results in his memory, and to develop in him a habit of reflecting and reasoning on his work. The quantitative work comprises volumetric processes only, and covers the most important of these. There are cuts of apparatus and an index.

The author disclaims in his preface any intention to make of the student an analytical chemist, his aim being to inculcate reflection and self-reliance, and to give a practical chemical knowledge through which the student can thoroughly master his profession. The book should be a useful one to those for whom it is intended.

ROBERT E. DIVINE.

**METHODS FOR THE ANALYSIS OF ORES, PIG IRON, AND STEEL.** In use at the Laboratories of Iron and Steel Works in the region about Pittsburg, Pa. Together with an appendix containing various special methods of analysis of ores and furnace products. Contributed by the chemists in charge, and edited by FRANCIS C. PHILLIPS. Second edition. Easton, Pa.: The Chemical Publishing Co., 1901. 170 pp. Price, \$1.00.

Probably in no manufacturing district in the world can there be found such a brilliant company of technical chemists as belong to Pittsburg, and its vicinity. Unfortunately for their brethren of other localities their work has been recorded almost exclusively in the *Proceedings of the Engineers' Society of Western Pennsylvania*. The publication of the first edition of this book came, therefore, as an exceedingly welcome event, and the second or present edition, containing as it does so much that is new and valuable, deserves and will get an even heartier appreciation. While eastern chemists have not come to a realizing sense of the superiority of barium hydroxide as an absorbent in the determination of carbon in steel, nor recognized the advantages of weighing over titrating the yellow precipitate in phosphorus determinations, there are nevertheless very many processes given whose value places them far beyond the possibility of difference of opinion. McKenna's wonderful method for chromium and chrome iron ores, his improved reductor, his delightfully easy and ingenious method of determining carbon in ferrochrome; Handy's noted method for phosphorus in newest form; Camp's clever method for phosphorus in coal, his valuable paper on phosphorus in ores and steel containing arsenic, his very convenient method of determining alumina; and Glass and Manby's simple and convenient volumetric method for tungsten. There are besides many original and ingenious little manipulative details. Occasions for criticisms are meager. There is to be noted, however, a very general disposition to ignore the precautions laid down by Blair in the determination of sulphur by the aqua regia method. It is the writer's experience that even more stringent ones are necessary. Again many of the western chemists have discontinued the use of Drown's method in determining silicon in pig iron. On account of titanium this would seem inadvisable even when the hydrofluoric treatment is used, and entirely inadmissible, of course, when this treatment is omitted.

This edition is well printed on good paper, and attractively



bound. Like its predecessor, it will find a place in every metallurgical laboratory.

GEORGE AUCHY.

LES CARBURES D' HYDROGÈNE, 1851-1901. RECHERCHES EXPERIMENTALES, par M. Berthelot. Three volumes. VOL. I.—ACETYLENE AND THE TOTAL SYNTHESIS OF HYDROCARBONS. VOL. II.—PYROGENIC HYDROCARBONS; VARIOUS SERIES. VOL. III.—THE COMBINATION OF HYDROCARBONS WITH HYDROGEN AND OXYGEN, THE ELEMENTS OF WATER. Paris: Gauthier-Villars. 1901.

The classic researches of Marcellin Pierre Eug. Berthelot upon the total synthesis of carbon compounds from their elements constitute the chief cornerstones of the beautiful and elaborate structure of modern synthetic organic chemistry. The appearance of the present publication, therefore, from the hand of the master, should be welcomed with deepest gratitude by every organic chemist. It is as unnecessary to recommend such a book to the student of organic chemistry, as it would be to recommend Shakespeare to a student of literature.

The work is not in any sense a treatise embodying all that is known about the hydrocarbons, but a collection and republication of the author's researches in this particular field. All of these investigations were conducted in the laboratory of the Collège de France, where the author made his début as "preparateur" (1851-1859), and where he has occupied a professorial chair since 1864. For over half a century he has made a study of these compounds, especially in the direction of their synthesis from the elements and of the effect of high temperatures upon them, publishing many hundred memoirs, notes, and notices, which are scattered through various scientific journals, more having appeared in the *Annales de Physique et de Chimie* than in any other single journal. These scattered articles have been gathered together and properly classified in the present work, so as to show clearly just how far each leading thought has been carried out experimentally.

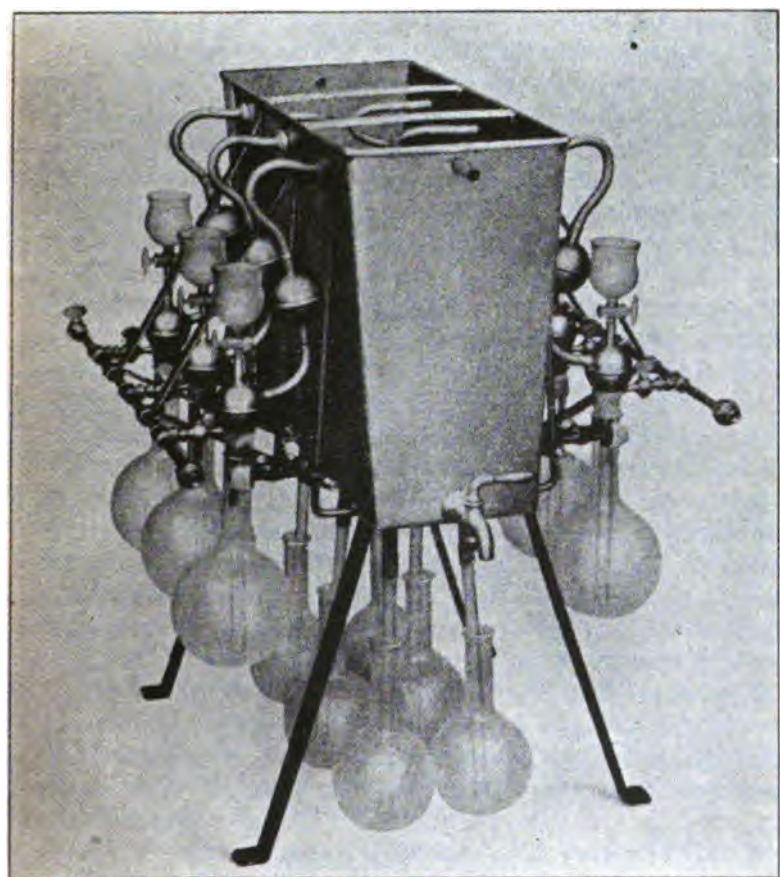
The subject-matter is arranged in seven books which are bound in three volumes.

Book 1 (263 pages) is divided into sections as follows: Section 1 (18 chapters) contains a description of the synthesis of acetylene from carbon and hydrogen; the details of its preparation and properties; its synthesis by the action of electric sparks upon simple gaseous compounds; studies of electrical equilibrium be-

tween carbon, hydrogen, acetylene; the various conditions for the formation of acetylene by incomplete combustion, by the action of red heat upon other hydrocarbons, etc.; its formation by the action of potassium hydroxide upon sulphonates; and, finally the synthesis of ethylene from acetylene. The recent work of Bone and Jerdan (*Proc. Chem. Soc.*, No. 240, page 162), is interesting in this connection. These authors find that in the electric arc, at a temperature of about  $1200^{\circ}\text{C}$ ., carbon and hydrogen unite with the production of small amounts of methane and ethane in addition to acetylene. Section 2 (6 chapters) is devoted to the polymers of acetylene, including the synthesis of benzene, styrene, and of the hydrides of naphthalene and of anthracene. Section 3 (8 chapters) contains the experiments made, mainly in collaboration with M. Vieille, upon the detonation of acetylene, a subject which is now one of considerable importance on account of the use of acetylene for illumination. Section 4 (4 chapters) describes the author's first experiments, begun in 1857, upon the synthesis of hydrocarbons, which were conducted before the discovery of the synthesis of acetylene, such being the production of methane from carbon bisulphide, the conversion by heat of methane into ethylene, ethane, propylene, etc., and the preparation of hydrocarbons from haloid ethers. Section 5 (2 chapters) records the synthesis of formic acid from carbon monoxide, and the resulting synthesis of hydrocarbons by the dry distillation of formates.

Book 2 (147 pages) treats of the derivatives of acetylene; its combinations with nitrogen, including the synthesis of hydrocyanic acid; its combinations with oxygen, resulting in the synthesis of acetic, glycollic, and oxalic acids, as well as phenol; its combinations with halogens, leading up to the synthesis of hexachlorobenzene; and, finally, certain of its metallic compounds.

Book 3 (352 pages). Section 1 (7 chapters). "The action of heat upon isolated hydrocarbons" begins with a table of the heats of formation of various hydrocarbons from their elements, the data which govern all transformations, and then records investigations of the action of heat upon methane, ethylene, benzene, and their homologues. These experiments form the sequel to the syntheses accomplished by the polymerization of acetylene. Section 2 (17 chapters). "The action of heat upon mixed hydrocarbons." This includes the action of





acetylene upon benzene, styrene, ethylene, and propylene, and pyrogenic synthesis of benzene homologues; the discovery and synthesis of acenaphthene; the study of various hydrocarbons contained in coal tar and of the styrene series; also, the first researches (1851) upon the pyrogenic products obtained from alcohol and from acetic acid, the first rough investigation of facts which found their interpretation in the light of experiments executed fifteen years later; the results obtained in 1858 upon the formation of hydrocarbons by the distillation of salts of the fatty acids, and containing more carbon than the fatty acid from which they were obtained, thus forming the sequel to the synthesis of hydrocarbons by the dry distillation of formates, the direct derivatives of carbon monoxide. The results of all these experiments are marshalled in support of a hypothesis upon the origin of hydrocarbons in the mineral kingdom, such, for example, as petroleum, which assumes the production of metallic carbides within the earth's crust, which then are decomposed by water, the hydrocarbons evolved being polymerized and reduced. This is essentially the hypothesis which has been favored by Moissan and by Mendeléeff. The theoretical laws governing the action of heat upon hydrocarbons, pure or mixed, are reviewed and deduced thermochemically. Section 3 (3 chapters). "The study of illuminating gas." The natural consequence of the foregoing investigations, which it corroborates in many points. Section 4 (6 chapters) deals with the analytical processes used in these investigations. Section 5 (1 chapter) considers the action of heat upon carbon monoxide; while Section 6 (2 chapters) records experiments made as to the action of the electric discharge upon carbon monoxide, pure or mixed with other gases, and upon hydrocarbons.

Book 4 (202 chapters). Section 1 (3 chapters), the production of allyl iodide by the reduction of glycerine, and the preparation from this of allyl isothiocyanate and sulphide. Also the preparation of propylene. Section 2 (5 chapters) treats of the isomerism of trimethylene and propylene, a type of what the author calls "dynamic isomerism." Section 3 (10 chapters) deals with the camphenes and their derivatives, showing their fundamental types, their synthesis and that of camphor, as well as the phenomena of dynamic isomerism which characterize the oil of turpentine.

Book 5 (288 pages) deals mainly with the reduction of hydrocarbons and includes the action of free hydrogen upon hydrocarbons, the retrosubstitution of halogen derivatives, and the general applicability of concentrated hydriodic acid as a powerful reducing agent for carbon compounds of all kinds, a method which was discovered by the author in 1857 and particularly investigated and developed by him in 1868.

Book 6 (80 pages) is devoted to studies upon the oxidation of hydrocarbons. It treats of the following topics: the oxidation of hydrocarbons in general; new methods for the synthesis of organic acids; the oxidation of allylene and of other hydrocarbons; the limited oxidation of hydrocarbons; the synthesis of bibasic acids from hydrocarbons; the oxidation of organic acids and of the benzene hydrocarbons; the use of potassium permanganate as an oxidizing agent; closing with a discussion of the camphors and the true function of ordinary camphor.

Book 7 (87 pages) is taken up with the experiments upon the synthesis of alcohols from hydrocarbons. It includes the synthesis of ordinary alcohol from ethylene, of isopropyl alcohol from propylene, of ethyl iodide from ethylene; the history of the synthesis of alcohols; the direct combination of olefines with hydracids; the synthesis of methyl, normal propyl, and isoamyl alcohols, and the isomerism of alcohols. Also, the characterization of alcohols by the direct formation of their esters, a method first applied successfully to borneol and cholesterine, whose structure was then unknown, and later to glycerine and the various saccharine principles, leading to the discovery of polyatomic alcohols and the establishment of the general system of classification for organic chemistry.

MARSTON TAYLOR BOGERT.

THE ELEMENTS OF QUALITATIVE ANALYSIS. BY W. A. NOYES, PH.D.  
Fifth Edition. New York: Henry Holt and Company. 1901. iv + 101 pp.  
Price, 80 cents.

The fifth edition of this book is practically the same as the fourth with the exception of that portion in which the detection of acids is considered. This part has been rewritten according to the methods proposed by Abegg and Herz, but their methods have been systematized, elaborated, and extended.

The book consists of an introduction dealing with the general

procedure such as precipitation, filtration, etc., and a discussion of that part of the theory of solutions relating to analytical operations; Part I, which deals with the systematic procedure for the detection of the metals, including a table of reactions of the various metals and acids with the usual reagents; Part II, which deals with the systematic analysis for the metals and the procedure for the analysis and detection of the acids; a special part which treats briefly of the qualitative analysis of water, iron, and gold and silver ores.

In regard to the introductory chapter it has been the experience of the reviewer that the theory of solutions relating to analytical chemistry cannot be properly taught by means of a chapter of this nature. It would seem to be much preferable to introduce the subject as the author has done, and then to present throughout the text examples *apropos* to the subject in hand, thus impressing upon the student's mind the applications and the significance of the theory. As it stands at present the student will be entirely absorbed by the "finding" of some particular element, and not upon the conditions by which this may be best accomplished.

Parts I and II are arranged practically according to the method originally adopted by Fresenius, which involves the use of numerous cross references and on this account is more or less confusing and is not so convenient as the direct statement of procedure. A noticeable omission is that of the Marsh test for arsenic which appears only in one of the tables of reactions and thus the enormous importance of this test is not emphasized. The method for the separation of calcium, barium, and strontium, while entirely satisfactory, is not so delicate as the ether alcohol method which has been shown to be very accurate.

The generally satisfactory nature of the book is indicated by the fact that it has already passed through four editions.

HENRY FAY.

THE LABORATORY COMPANION TO FATS AND OILS INDUSTRIES. BY DR. J. LEWKOWITSCH, M.A., F.I.C. London: Macmillan and Co. 1901. xi + 147 pp. Price, six shillings.

With the exception of five pages of introductory matter this volume consists of tables. For methods of work and for full explanation of the tables, one must refer to the author's "Chemical Analysis of Oils, Fats, and Waxes," second edition, 1898.

The work is divided into three parts, dealing with : 1. System and Examination of Fats and Waxes; 2. Fats, Oils, and Waxes, and the Commercial Products Derived Therefrom ; and 3. General Tables. Part 2 includes the greater part of the work and is divided into two parts, A, containing the constants and variables of the oils and waxes, and B, dealing, in eight sections, with the commercial products of the fats and oils industry.

While these tables follow, in a general way, the lines laid down in the author's "Chemical Analysis," one finds on examination much additional matter in the tables, such as the constants of varnish gums and the detailed information regarding commercial driers.

The author has brought together a great mass of facts and has arranged them in an attractive and convenient form. The book is well indexed and deserves a place both in the technical reference library and in the working laboratory. H. A. HUSTON.

---

#### BOOKS RECEIVED.

Lectures on the History of the Development of Chemistry from the Time of Lavoisier. By A. Ladenburg. Translated from the Second German Edition by Leonard Dobbin, Ph.D. (With additions and corrections by the author.) Edinburgh : Published by the Alembic Club. Edinburgh Agent : Wm. F. Clay ; London Agents : Simpkin, Marshall, Hamilton, Kent & Co., Ltd. 1900. xvi + 373 pp.

The Elements of Qualitative Analysis. By Wm. A. Noyes, Ph.D. Fifth Edition, Revised. New York : Henry Holt & Co. 1901. 101 pp. Price, 80 cents.

Studies in Bread and Bread-Making at the University of Minnesota in 1899 and 1900. By Harry Snyder. Washington : Government Printing Office. 1901. 65 pp.

Reclamation of Salt Marsh Lands. Circular No. 8, U. S. Department of Agriculture, Division of Soils, Washington, D. C. 10 pp.

A Manual of Volumetric Analysis. Treating on the Subjects of Indicators, Test-Papers, Alkalimetry, Acidimetry, Analysis by Oxidation and Reduction, Iodometry, Assay Processes for Drugs with the Titrimetric Estimation of Alkaloids, Estimation of Phenol, Sugar, Tables of Atomic and Molecular Weights. By Virgil Coblentz, Ph.D., Pharm.M., F.C.S. Illustrated. Philadelphia : P. Blakiston's Son & Co. 1901. 181 pp. Price, \$1.25.

The Practical Methods of Organic Chemistry. By Ludwig Gattermann. Translated by William B. Schober. Authorized Translation. The Second American from the Fourth German Edition. With numerous illustrations. New York : The Macmillan Co. 1901. xiv + 360 pp.



**An Introduction to Chemical Analysis.** For Students of Medicine, Pharmacy, and Dentistry. By Elbert W. Rockwood, M.A., M.D. Illustrated. Philadelphia: P. Blakiston's Son & Co. 1901. 255 pp. Price, \$1.50, net.

**Exhaustion and Abandonment of Soils.** Testimony of Milton Whitney, Chief of Division of Soils, before the Industrial Commission. Report No. 70, U. S. Department of Agriculture, Washington, D. C. 48 pp.

**A Soil Study, III. The Soil.** By William P. Headden. Bulletin No. 65. The Agricultural Experiment Station of the Agricultural College of Colorado, Fort Collins, Colo. 1901. 56 pp.

**The Bulletin of the North Carolina State Board of Agriculture,** Raleigh, N. C. October, 1901. 31 pp.

**Modern Chemistry. First Part, Theoretical.** By William Ramsay, D.Sc. New York: The Macmillan Co. 1901. Cloth. 16mo. 127 pp. Price, 40 cents.

**Modern Chemistry. Second Part, Systematic.** By William Ramsay, D.Sc. New York: The Macmillan Co. 1901. Cloth. 16mo. 207 pp. Price, 40 cents.

**Digest of Criticisms on the United States Pharmacopoeia: Seventh Decennial Revision (1890).** Published by the Committee on Revision of the Pharmacopoeia of the United States of America (1900-1901). Part III. Chairman of the Committee: Joseph P. Remington, Ph.M., 1832 Pine St., Philadelphia, Pa. 8vo. 181 pp.

**Methods for Analysis of Ores, Pig Iron, and Steel in Use at the Laboratories of Iron and Steel Works in the Region about Pittsburg, Pa., together with an Appendix Containing Various Special Methods of Analysis of Ores and Furnace Products.** Contributed by the chemists in charge and edited by Francis C. Phillips. Second Edition. Easton, Pa.: The Chemical Publishing Co. 1901. vii + 170 pp. Price, \$1.00, net.

**Studies from the Chemical Laboratory of the Sheffield Scientific School** Edited by Horace L. Wells. Vol. I. xi + 444 pp. Vol. II. ix + 379 pp. New York: Charles Scribner's Sons. 1901. Price, \$7.50 per set.

**A Laboratory Guide to the Study of Qualitative Analysis.** By E. H. S. Bailey, Ph.D., and Hamilton P. Cady, A.B. Fourth Edition. Philadelphia: P. Blakiston's Son & Co. 1901. 234 pp. Price, \$1.25, net.

**Studien zur Kenntnis der Abhängigkeit der Viscosität der Flüssigen Körper von der Temperatur und von ihrer chemischen Constitution.** Abt. I. Von Alexius Batschinski. Aus Bull. d. Nat. de Moscou, No. 1, 1901. 99 pp.

**Vorlesungen über theoretische und physikalische Chemie.** Von J. H. van 't Hoff. Erstes Heft. Die chemische Dynamik mit in den Text eingedruckten Abbildungen. Zweite Auflage. Braunschweig: Friedrich Vieweg und Sohn. 1901. xi + 251 pp. Price, 6 marks.

**On the Composition of Dutch Butter.** By Dr. J. J. L. van Ryn. London: Ballière, Tyndall and Cox. 1902. 55 pp.

**Annuaire pour l'an 1902.** Publié par le Bureau des Longitudes. Avec des

Notices scientifiques. Paris : Gauthier-Villars, Quai des Grands-Augustins, 55. Price, 1.5 francs.

The Bulletin of the North Carolina State Board of Agriculture, Raleigh, N. C. November, 1901. 36 pp. December, 1901. 20 pp.

Outlines of Electrochemistry. By Harry C. Jones, Assistant Professor of Physical Chemistry in Johns Hopkins University. New York : D. Van Nostrand Co. 1901. vi + 106 pp. Price, \$1.50.

The San José Scale-Insect : Its Appearance and Spread in Connecticut. Bulletin No. 135, Connecticut Agricultural Experiment Station, New Haven, Conn. 14 pp. 5 plates.

Report of the Connecticut Agricultural Experiment Station for the Year Ending October 31, 1901. Part I. Fertilizers. 101 pp.

Fourteenth Annual Report of the Agricultural Experiment Station, University of Illinois, Urbana, Ill., 1900-1901. 17 pp.

Individual Differences in the Value of Dairy Cows, 14 pp. Bull., 66; Apple Scab, 48 pp., Bull. 67; Important Details of Spraying, 32 pp., Bull. 68, University of Illinois, Agricultural Experiment Station, Urbana, Ill.

# THE JOURNAL

OF THE

## AMERICAN CHEMICAL SOCIETY.

---

### ON THE INHIBITION OF CHEMICAL REACTIONS BY FOREIGN SUBSTANCES. I.

By S. W. YOUNG.

Received January 17, 1902.

[N a recent paper<sup>1</sup> attention was called to some very curious phenomena which showed themselves in the oxidation of solutions of stannous chloride by means of free oxygen. These phenomena consist in very marked reduction of the rate of the oxidation as a result of the presence of relatively small quantities of poisonous substances, especially alkaloids. It was, however, seen that potassium cyanide also possessed this power.

It was thought well to delay the further investigation of these curious actions until the course of the reaction between stannous chloride and free oxygen was somewhat more thoroughly understood. The attempt to follow the course of the reaction was successful,<sup>2</sup> but unfortunately, the result was to show that the reaction was complex, taking place in two stages, and on account of this complication, little suited to the investigations in question. It was, therefore, thought advisable to choose another reaction, provided one could be found which would be sensitive to these peculiar agencies.

A solution of arsenic trioxide in water was first tried, but

<sup>1</sup> This Journal, 23, 140.

<sup>2</sup> *Ibid.*, 23, 450.

neither in acid, neutral nor alkaline solution was its oxidation rate sufficiently great to allow of its being used without enormous loss of time. Nor was sufficient acceleration produced by previously treating the solution with hydrogen sulphide or after boiling it for some time with arsenic sulphide.<sup>1</sup> The same difficulty was found with ferrous sulphate. Several other substances were tried, but their oxidation rates were found to be either too high (in which case the rate of oxidation is not independent of the action of the apparatus) or too low. Finally a solution of sodium bisulphite was tried and this gave more hopeful indications. The sodium bisulphite used was a commercial product and probably not very pure. Twenty-five cc. of a solution of this substance, of unknown strength, were placed in the shaking apparatus<sup>2</sup> at 25° C. This showed an oxidation rate of 0.2 cc. in three minutes. A trace of copper sulphate raised this to 0.3 cc. in two minutes, and finally the addition of a small quantity of ferrous sulphate raised the rate to 0.5 cc. in one minute. While the absorption was progressing at this last rate, a small quantity of a brucine hydrochloride solution was injected. From this point on the results are given in the following table. In this table  $T$  = time in minutes ( $T = 0$  = time of injection of brucine).

$V$  = Volume reading on the gas burette.

$\frac{\Delta V}{\Delta T}$  = Average absorption per minute in each interval of observation.

$T =$	0	1	2	3	4	5	6
$V =$	45.5	42.50	40.80	40.00	39.70	39.55	39.45
$\frac{\Delta V}{\Delta T} =$	....	3.00	1.70	0.80	0.30	0.15	0.10
$T =$	7	9	10	15	20	30	38
$V =$	39.40	39.34	39.30	39.05	38.80	38.35	38.00
$\frac{\Delta V}{\Delta T} =$	0.05	0.03	0.04	0.05	0.5	0.045	0.044

At  $T$  = thirty-eight minutes, the shaking was discontinued for twenty-two hours. During this time 10.2 cc. had been absorbed. On shaking, the following results were obtained :

$T =$	0	90.
$V =$	27.8	26.60
$\frac{\Delta V}{\Delta T} =$	...	0.013

<sup>1</sup> See Mohr : "Titrimethode," 1886, p. 364; also Young : This Journal, 23, 143-144.

<sup>2</sup> This Journal, 23, 119.

Further observations were made with this solution, which need not be recorded here. Gradual reduction of the rate of absorption was noted, due mainly, of course, to the gradual decrease in the concentration of bisulphite.

The results of this first experiment are given here in detail because they afford a good illustration of several of the phenomena to which this paper is devoted. They are: (1) acceleration by means of salts of copper and iron; (2) an initial acceleration upon adding a small quantity of brucine hydrochloride; (3) the rather rapid decrease of the reaction rate thereafter, to a very small value. As the bisulphite showed the phenomena sought in so satisfactory a manner, considerable time has been devoted to its study. It was, however, thought best to use the neutral sulphite as the basis of the solutions studied, as this could be studied equally well in acid, neutral or alkaline solution.

Before passing to a study of the results which are given in the following paper, I wish to suggest a terminology, which must, of course, be considered as subject to change. The phenomena involved are almost wholly new, and something of the sort seems necessary. Bredig,<sup>1</sup> working in a somewhat analogous field, has used the word "poisoning" (*Vergiftung*) to describe the effect of poisons upon the rate of catalysis by colloidal platinum and gold solutions.

In view of the apparently rather broad analogy existing between physiological poisoning and the phenomena in question one might be almost tempted to follow this usage in the present case. After some thought, it seems to me, however, that such usage is scarcely justifiable at present. In the first place, it is by no means true that the retarding actions under consideration are confined to physiological poisons; and in the second place it is by no means certain that the analogy, in general, is more than superficial. Under these conditions it would seem that the application of the concept of "poisoning" to an entirely new domain is likely to lead to confusion, useless speculation and to superficiality in the investigation of the field. I will, therefore, use the word "inhibition" to cover the phenomena in point, this word having, so far as I am aware, no present technical significance in chemistry. An "inhibitive agent" is then a substance producing an "inhibition," or having an "inhibitive effect." For the

<sup>1</sup> Bredig and Müller von Berneck: *Ztschr. phys. Chem.*, 31, 258, and later papers.

period beginning with the addition of the inhibitive agent and ending with the time when the inhibitive influence reaches its maximum the true period of development of the inhibition, or more simply, the "development period" will be used. The introduction of these terms, at least for present use, seems to me to be justifiable. The phenomena may naturally be included under the general head of negative catalysis.

It may be stated here that the results following lay no claim to being more than roughly quantitative. No special precautions were taken to purify the distilled water used, and as Bigelow<sup>1</sup> has shown, the character of the distilled water used has a considerable influence upon the rate of oxidation. The object has been solely to study the general character of the phenomena and their scope.

#### I. THE APPARATUS.

The apparatus used was a modification of the one used in the studies with stannous chloride. The chief modification

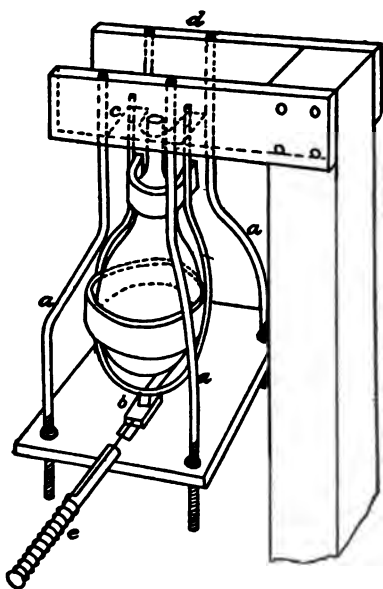


Fig. 1.

is of sufficient importance to be sketched here. It lies wholly in the shaking part of the machine. Whereas this in the old machine<sup>2</sup> was fastened in the thermostat tank, in the new one it is wholly independent of this. The great advantage lies in the avoidance of the jarring and shaking of the thermostat, which sometimes, in the old machine, threatened to fall from its supports, and required constant vigilance. The new apparatus will run indefinitely without attention. The new arrangement is shown in Fig. 1. It

consists of a stout wooden stand which can be raised and lowered at will. In the two horizontal arms of this stand are fixed four stout rods of  $\frac{1}{4}$  inch brass, *a, a, a, a*, which are

<sup>1</sup> *Ztschr. phys. Chem.*, 26, 493.

<sup>2</sup> *This Journal*, 23, 121.

doubly curved as in the drawing. The lower ends of these rods are threaded for a distance of about 4 inches. Upon these rods is supported a rectangular brass plate,  $\frac{1}{8}$  inch thick, with  $\frac{1}{4}$  inch holes at each corner. This platform is fastened to the rods by means of two nuts on each rod, one above and one below the plate. These, when screwed tight, hold the platform very firmly in place, and furthermore allow of adjusting the height of the platform, as may be desired.

Down the middle of the platform longitudinally is cut a slot in which runs a small carriage, *b*, also of brass. This slides freely back and forth in the slot, and is provided with a simple device for attaching the bottom of the carrier in which is held the flask. This carrier is the same as was used in the experiments with stannous chloride. The brass rods at the top of this carrier pass through holes in the brass plate *c* which is fastened to one of the horizontal arms of the wooden stand. The whole carrier and flask are thus easily removable from the apparatus. The shaking is brought about by an electric motor with variable resistance to regulate speed. A stout gut cord passes from the crank of the motor over a pulley fastened on the back of the far arm of the wooden stand (near *d*), thence downward under a second pulley (not shown) fastened at the far end of the brass platform. Thence it runs to the carriage *b*, to which it is fastened. The return of the flask to its original position after being pulled to the far end of the platform, is brought about by the spiral spring *e* of hardened brass wire. As a matter of fact, two such springs are used, one fastened to the carrier above, and the other below the platform. This insures more even working of the carriage in the slot. Simple devices allow of the regulation of the length of stroke, and of the tension of the springs. Having once gotten the apparatus in order, I have used it for nearly four months, almost daily, and some times for eight hours per day, without the necessity for the slightest repair or alteration, except that one gut string had to be replaced.

The method used in the following experiments was the same as was used in the studies with stannous chloride, and for further details the reader must be referred to that paper.

## 2. SCOPE OF THE PHENOMENON OF INHIBITION.

So far as I am aware almost all reactions which have hereto-

fore shown the phenomenon of inhibition, *i. e.*, a marked reduction of the reaction rate under the influence of minute quantities of foreign substances, are reactions in which free oxygen is concerned in some way or other. Exceptions are apparently to be found in some cases, in the action of enzymes.

The reactions which are of the greatest importance for us here may be divided into two groups: (1) reactions in which hydrogen peroxide is decomposed with the evolution of free oxygen; (2) the voluntary (and catalytically accelerated) oxidation of certain substances by free oxygen. The literature bearing upon the first group has been brought together and materially extended by Bredig and his coworkers.<sup>1</sup>

In this group we have to do always with a deadening of the efficiency of a positive catalysor or accelerator. Among these catalysors we find certain organic ferments, platinum foil and black and colloidal platinum and gold solutions. The accelerating action of these substances is greatly diminished by the addition of minute quantities of a great variety of substances, including hydrogen sulphide, carbon bisulphide, hydrocyanic acid, mercuric chloride, etc. The catalytic action of the blood corpuscles is also reduced by minute traces of hydrocyanic acid. Bredig<sup>2</sup> states that strychnine is apparently without action in the catalysis of hydrogen peroxide by means of colloidal platinum.

In the second group we have to do with reactions in some cases, which are apparently not catalytically accelerated in the first place, *i. e.*, with a true negative catalytic effect.<sup>3</sup> All such cases, so far as I know, are reactions of oxidation by means of free oxygen. Among these are to be mentioned: (1) the influence of small quantities of foreign substances in oxygen upon the glowing of phosphorus;<sup>4</sup> (2) the phenomena observed by Bigelow<sup>5</sup> in connection with the oxidation of sodium sulphite by the oxygen of the air; (3) the phenomena involved in the oxidation of stannous chloride by means of oxygen.<sup>6</sup> A case of reduction of

<sup>1</sup> Bredig and Müller von Berneck: *Loc. cit.*; Bredig and Ikeda: *Ztschr. phys. Chem.*, 37, 1; Bredig and Reinders: *Ibid.*, 37, 323.

<sup>2</sup> *Loc. cit.*

<sup>3</sup> We may, for convenience, distinguish between "apparent" negative catalysis, or the reduction of the activity of a positive catalysor, and "true" negative catalysis, or the reduction of the rate of a reaction occurring without previous catalytic acceleration.

<sup>4</sup> The literature of this subject together with new results is to be found in a paper by Centnerswer: *Ztschr. phys. Chem.*, 26, 1.

<sup>5</sup> Bigelow: *Ibid.*, 26, 493.

<sup>6</sup> *Loc. cit.*



reaction rate in an already catalytically accelerated oxidation was found by Ernst<sup>1</sup> in the oxidation of hydrogen by oxygen in presence of a colloidal platinum solution. The same phenomenon with platinum foil was observed by Faraday.

In order to gain some idea of the scope of these inhibitive actions in the oxidation of sodium sulphite, several experiments were carried out by me upon the oxidation by means of agents other than oxygen. The substances chosen were nitrous and nitric oxides; both being gases, the phenomena allowed of being studied in the apparatus with which I was working.

*a. Experiments with Nitrous Oxide.*—The experiments with nitrous oxide were carried out exactly according to the method described in the previous paper<sup>2</sup> for studying the oxidation of stannous chloride. The nitrous oxide was prepared from ammonium nitrate and stored for use in a gas-holder. On beginning the experiment, a very marked decrease in the volume of the gas in the burette was noticed, due, of course, to the solubility of nitrous oxide in the solution. After this first rapid absorption had ceased, measurements were begun. After a time a quantity of brucine hydrochloride solution was added and measurements continued. The results of two series of measurements are given below. In the first series water was used in the gas burette. As it was thought that the slow decrease in volume might possibly be due to gradual absorption of the gas by the water in the burette, mercury was used in the second experiment, and this was, furthermore, allowed to stand for a couple of days after the measurements were discontinued in order to see to a certainty whether a reaction really occurred. *T* is given in minutes.

## EXPERIMENT I.

				1 cc. $\frac{m}{10}$ brucine hydrochloride added. <sup>3</sup>			
$T =$	0	10	20	30	0	10	20
$V =$	36.2	35.85	35.5	35.2	35.45	35.10	34.75
$\frac{\Delta V}{\Delta T} =$	....	0.035	0.035	0.035	....	0.035	0.035

After making the solution slightly acid the rate of absorption remained unchanged.

<sup>1</sup> Ernst: *Ztschr. phys. Chem.*, 37, 448.

<sup>2</sup> *Loc. cit.*

<sup>3</sup> *m* is used here to represent the molecular or "molar" weight. *Cf.* Noyes: *This Journal*, 23, 41.

## EXPERIMENT 2.

	Mercury in gas burette.				1 cc. $\frac{m}{10}$	brucine hydrochloride added.		
$T =$	0	5	10	15	0	5	10	
$V =$	39.7	39.55	39.40	39.20	39.35	39.15	38.95	
$\Delta V$	...	0.03	0.03	0.04	...	0.04	0.04	
$\Delta T$								

The volume after standing for twenty-four hours had decreased to 28.2 cc. After forty-eight hours to 19.3 cc. Thus during the whole time over 20 cc. of the gas had been absorbed, which shows conclusively that a reaction of some sort takes place. The evidence of both sets of observations goes to show, however, that the rate of this reaction is not measurably influenced by the addition of the indicated amount of brucine hydrochloride solution. The sulphite solution used in these experiments contained 2.5 grams of crystallized sulphite per 100 cc. of solution. As will be shown later the amount of brucine used here would have sufficed in case of oxidation with oxygen to have reduced the rate to  $\frac{1}{10}$ , or less, of its original value. The conclusion would seem to be justified that the reaction between nitrous oxide and sodium sulphite is uninfluenced by brucine.

*b. Experiments with Nitric Oxide.*—The first few attempts to follow the reaction between sodium sulphite and nitric oxide showed that the reaction goes too rapidly to be measured with certainty in the apparatus in use, and the same was found true of stannous chloride. A 0.2 normal solution of stannous chloride absorbed the gas at the rate of about 25 cc. per minute. No measurable influence was exerted by the addition of relatively large quantities of brucine hydrochloride. A solution of 5 grams of sodium sulphite in 200 cc. of solution gave approximately the same result. With such rapid absorption it is probable that it is more nearly the absorption rate than the oxidation rate that is measured. By using a solution only one-half as strong as the above, the rate was still too rapid for certainty. The results of such a series is given here. As will be seen the addition of the brucine hydrochloride has again no noticeable effect. Time in minutes:

Added 1 cc. $\frac{m}{10}$ brucine hydrochloride.										
$T =$	0	$\frac{1}{2}$	1	$1\frac{1}{2}$	$2\frac{1}{2}$	$3\frac{1}{2}$	$4\frac{1}{2}$	$6\frac{1}{2}$	$7\frac{1}{2}$	10
$V =$	47.0	40.7	36.7	33.2	26.4	17.7	9.9	20.6	20.5	20.4
$\Delta V =$	...	6.3	4.0	3.5	6.8	8.7	7.8	-10.7	+0.1	+0.1

An inspection of these results shows no appreciable drop in the reaction rate upon addition of the brucine hydrochloride, or at least none in any way comparable with the drop noticed (see later) in results with oxygen. A most marked feature of the results is seen in the fact that the gas volume at first rapidly decreases, then increases very rapidly and finally very slowly decreases again. Several experiments showed this to be a constant phenomenon and use was made of it to determine, if possible, an influence of the alkaloid upon the rate or course of the reaction. Several series of observations were made upon solutions without addition of brucine hydrochloride and several with addition of this reagent. *T* in minutes:

*a. Results without Brucine.*

1.			2.			3.			4.		
<i>T.</i>	<i>V.</i>	$\Delta V.$	<i>T.</i>	<i>V.</i>	$\Delta V.$	<i>T.</i>	<i>V.</i>	$\Delta V.$	<i>T.</i>	<i>V.</i>	$\Delta V.$
0	49.0	....	0	50.0	....	0	46.5	....	0	50.0	....
$\frac{1}{2}$	39.0	+10.0	$\frac{1}{2}$	45.0	+5.0	$\frac{1}{2}$	37.5	+9.0	$\frac{1}{2}$	39.0	+11.0
1	32.5	+6.5	1	42.0	+3.0	1	32.5	+5.0	1	30.5	+8.5
$1\frac{1}{2}$	26.0	+6.5	$1\frac{1}{2}$	38.5	+3.5	$1\frac{1}{2}$	27.0	+5.5	$1\frac{1}{2}$	22.5	+8.0
2	20.5	+6.5	2	35.5	+3.0	2	22.0	+5.0	2	16.5	+6.0
$2\frac{1}{2}$	15.5	+5.0	$2\frac{1}{2}$	30.0	+5.5	$2\frac{1}{2}$	18.0	+4.0	$2\frac{1}{2}$	14.2	+2.3
3	11.2	+4.3	3	25.4	+4.6	3	14.0	+4.0	3	21.5	-7.3
$3\frac{1}{2}$	8.0	+3.2	$3\frac{1}{2}$	22.4	+3.0	$3\frac{1}{2}$	10.8	+3.2	$3\frac{1}{2}$	22.4	-0.9
$3\frac{3}{4}$	6.5	+1.5	4	20.5	+1.9	4	8.5	+2.3	4	22.3	+0.1
$4\frac{1}{4}$	11.0	-4.5	$4\frac{1}{2}$	17.3	+3.2	$4\frac{1}{2}$	10.0	-1.5	5	22.2	+0.1
$4\frac{3}{4}$	19.0	-8.0	5	15.2	+2.1	5	20.0	-10.0			
5	21.4	-2.4	$5\frac{1}{2}$	17.5	-1.8	$5\frac{1}{2}$	21.0	-1.0			
6	21.1	+0.3	6	25.5	-8.5	8	20.6	+0.4			
8	20.9	+0.2	$6\frac{1}{2}$	25.8	-0.3	10	20.5	+0.1			
			7	25.65	+0.15	35	19.8	+0.7			
			8	25.4	+0.25	42 hrs. 5.1	+14.7				

*b. Results with Brucine Hydrochloride.*—In these experiments, the brucine hydrochloride was added before beginning the experiment. One cc. of  $\frac{m}{10}$  brucine hydrochloride was used.

1.			2.			3.		
<i>T.</i>	<i>V.</i>	$\Delta V.$	<i>T.</i>	<i>V.</i>	$\Delta V.$	<i>T.</i>	<i>V.</i>	$\Delta V.$
0	50.0	....	0	50.0	...	0	50.1	....
$\frac{1}{2}$	43.0	+7.0	$\frac{1}{2}$	38.0	+12.0	$\frac{1}{2}$	38.0	+12.0
1	37.0	+6.0	1	31.0	+7.0	1	26.0	+12.0
$1\frac{1}{2}$	31.0	+6.0	$1\frac{1}{2}$	26.0	+5.0	$1\frac{1}{2}$	19.0	+7.0
2	25.7	+5.3	2	24.5	+1.5	2	24.0	-5.0
$2\frac{1}{2}$	21.5	+4.2	$2\frac{1}{2}$	23.5	+1.0	$2\frac{1}{2}$	29.5	-5.5
3	19.0	+2.5	3	23.1	+0.4	3	29.6	-0.1
$3\frac{1}{2}$	28.0	-9.0	$3\frac{1}{2}$	26.0	-2.9	5	29.4	+0.2
4	28.3	-0.3	4	30.9	-4.9			
5	28.2	+0.1	5	30.6	+0.3			

In the experiments without brucine hydrochloride, the turning-point in the volume reading occurred after respectively  $3\frac{1}{2}$ , 5.4, and  $2\frac{1}{2}$  minutes. With brucine, after respectively 3, 3, and  $1\frac{1}{2}$  minutes. Without brucine hydrochloride, the turning-point occurred after the following volumes had been absorbed: 42.5 cc., 34.8 cc., 38 cc., and 35.8 cc.; with brucine hydrochloride, after respectively 31 cc., 27 cc., and 31 cc. had been absorbed.

The variations in all these results are undoubtedly due mainly to variations in the rate of shaking and in variations in local conditions, such as slight differences in the form of the flasks used, which might make much difference in the surface of the liquid exposed and consequently, at these high rates, in the oxidation rate. On the whole there are no more marked variations between the two series than between different experiments of either series, and the conclusion seems to be justifiable that the brucine hydrochloride exerts no influence upon the rate of the reaction, or if it does that its influence is of a wholly different order of magnitude from the influence exerted upon the oxidation by means of free oxygen.

Thus the evidence at hand seems to point rather distinctly toward the probability that the inhibitory actions in question are quite closely confined to reactions in which free oxygen is involved. Of course this point cannot be considered as definitely settled until a vastly greater amount of evidence is accumulated.<sup>1</sup>

### 3. PRELIMINARY EXPERIMENTS TO DETERMINE WHAT CLASSES OF SUBSTANCES SHOW INHIBITIVE ACTION.

A large number of experiments were carried out to determine how wide-spread the phenomenon of inhibition of the reaction between oxygen and sodium sulphite solution might be. The method of experimentation was to place 25 cc. of the sulphite

<sup>1</sup> The anomalous conduct of the reaction with nitric oxide and sodium sulphite is readily explained upon the assumption that the nitric oxide at first reacts with the sulphite, forming an unstable compound which then rather rapidly breaks down with the evolution of some other gas. The final slow decrease in volume may be due merely to a residue of the original reaction between the much diluted reagents, or it may be due to the fact that the gas evolved is some substance capable of further reaction. In looking up the literature on this matter we find that nitric oxide, when conducted into an alkaline solution of sodium sulphite, yields nitrosohydroxylamine sulphonic acid in form of the sodium salt  $\text{Na}_2\text{SN}_2\text{O}_5$ . (Raschig: *Ann. Chem. (Liebig)*, 241, 230.) These salts show a tendency to decompose into sulphates and nitrous oxide. Several experiments made in my laboratory by Mr. Bruno Olshausen show that the ratio between the volume of nitric oxide absorbed and the volume of the gas given off is very nearly 2:1. The phenomena referred to above are thus readily explained, since, as has been previously shown, nitrous oxide itself seems to be slowly absorbed by sodium sulphite solutions.

solution in the flask of the shaking apparatus, to determine the rate of oxidation before any foreign substance was added, then to add an amount of the substance to be tested sufficient to make the solution approximately  $\frac{1}{100}$  molar. Usually 1 cc. of a  $\frac{1}{100}$  molar solution was used for this purpose. The solutions of sodium sulphite used from his point on were always prepared by dissolving 2.5 grams of the crystallized salt in 200 cc. of distilled water. These solutions were approximately  $\frac{1}{100}$  normal. For this particular investigation, a knowledge of the exact strength of the solutions was wholly unnecessary. It was considered wise to prepare a fresh solution about every two hours, mainly because of the rather marked change in the oxidation rate of the solution on standing. The flasks used were cleaned after each experiment by soaking in chromosulphuric acid mixture. This was found necessary, as after simple washing with water, no matter how carefully done, there seemed to remain always enough of the foreign substance to throw out the results of the following set of observations. In working in neutral and alkaline solutions air was used instead of pure oxygen on account of the too rapid rate of oxidation with the latter.

*a. Experiments with Brucine Hydrochloride.*

The first substance investigated was brucine hydrochloride. This was found to possess a most marked inhibitive action in neutral solution, as the following measurements show (time in minutes):

I			
Before adding brucine hydrochloride.			After adding brucine hydrochloride.
$T = 0$	$1$	$2$	$0$ $1$ $2$ $3$
$V = 49.25$	$47.90$	$46.60$	$46.20$ $46.05$ $45.95$ $45.85$
$\Delta V = \dots$	$1.35$	$1.30$	$\dots$ $0.15$ $0.10$ $0.10$
$\Delta T = \dots$	$1.35$	$1.30$	$\dots$ $0.15$ $0.10$ $0.10$
2			
$T = 0$	$1$	$2$	$3$
$V = 50.00$	$48.50$	$48.50$	$48.40$ $48.3$ $48.22$
$\Delta V = \dots$	$1.50$	$\dots$	$\dots$ $0.10$ $0.10$ $0.08$
$\Delta T = \dots$	$1.50$	$\dots$	$\dots$ $0.10$ $0.10$ $0.08$

In slightly alkaline solution, the inhibitive action of brucine hydrochloride is vastly greater than in neutral solution. This is shown by the following experiment in which such a weakly alkaline solution was used, the concentration of brucine hydrochloride being the same as above; *viz.*,  $\frac{1}{300}$  molar.

Before adding brucine hydrochloride.				After adding brucine hydrochloride.			
$T =$	0	1	2	0	1	2	17 hours.
$V =$	50.00	48.60	47.45	46.90	46.90	46.90	46.90
$\Delta V$	....	1.40	1.15	....	0.00	0.00	0.00
$\frac{\Delta V}{\Delta T} =$							

That is, after seventeen hours, no measurable oxidation had taken place.

This enormous increase of inhibitive action in alkaline over neutral solution is, perhaps, even more strikingly shown in the following set of observations. In this case, the original solution was neutral and, after determining the normal rate, 1 cc. of a 0.0001 molar solution of brucine hydrochloride was added. This made the solution finally  $\frac{1}{200,000}$  molar in brucine. The result, as will be seen, was an extremely small, if any, reduction of the oxidation rate. Next, a few drops of dilute potassium hydroxide solution were added. The enormous drop in the rate upon this may be seen from the figures:

Before adding brucine hydrochloride.			After adding brucine hydrochloride.			After adding potassium hydroxide.		
$T.$	$V.$	$\frac{\Delta V}{\Delta T}.$	$T.$	$V.$	$\frac{\Delta V}{\Delta T}.$	$T.$	$V.$	$\frac{\Delta V}{\Delta T}.$
0	50.00	...	0	44.90	...	0	41.40	....
1	47.50	2.50	1	43.00	1.90	1	41.20	0.20
2	45.30	2.20	2	41.60	1.40	50	40.94	0.005
						40 hours	39.75	0.016

As will be seen the rate is reduced to something less than 0.01 of the normal rate by the presence in alkaline solution of a quantity of brucine hydrochloride of the concentration of  $\frac{1}{200,000}$  molar.

In acid solution the influence of brucine hydrochloride is much less than in neutral solution and the period of development of the inhibition is much longer. The oxidation in weakly acid solution takes place very slowly and in most of the experiments under these conditions, the reaction was accelerated by means of a few drops of a solution of mixed copper and iron sulphates. The whole phenomenon in acid solution is quite complex and could be given here only with the aid of many words. The discussion of this point will be left therefore until later.

#### *b. Experiments with Quinine Bisulphate.*

Quinine was the next alkaloid studied and it was used in the form of the bisulphate. Some objection attaches to the use of an acid salt for this purpose, since the presence of free hydrogen

ions markedly influences the reaction rate, and since further the influence of quinine in acid solution is also much less than in neutral or alkaline solution. Still the influence even with the acid salt is so clear and sharply defined as to leave the matter in no sort of doubt. I give here only a limited number of measurements to illustrate the action of quinine bisulphate. Many more were made, but there is no particular need of giving them here, as the same phenomenon was always observed under the same conditions.

The following figures show the influence of quinine bisulphate in neutral solution. The quantity of the alkaloid added was 1 cc. of a 0.1 molar solution, thus making the whole solution  $\frac{1}{200}$  molar.

Before.			After.					
T.	V.	$\frac{\Delta V}{\Delta T}$	T.	V.	$\frac{\Delta V}{\Delta T}$	T.	V.	$\frac{\Delta V}{\Delta T}$
0	45.00	...	0	44.10	...	6	41.10	0.52
1	44.18	0.82	1	43.70	0.40	7	40.64	0.46
			2	43.22	0.48	8	40.18	0.46
			3	42.70	0.52	9	39.75	0.43
			4	42.16	0.54	10	39.30	0.45
			5	41.62	0.54			

As will be seen there is at first a very marked reduction, to a little less than one-half. The rate, however, increases noticeably for about five minutes. The cause of this was easily found. After the experiment was discontinued, the solution in the flask was found to contain a considerable quantity of a glittering white crystalline substance. This is probably a very slightly soluble compound of quinine with sodium sulphite. Brucine shows the same phenomenon but to a very much smaller degree. The explanation of the increasing absorption rate is, however, readily explained since there is formed first a solution supersaturated as to the quinine compound. This then gradually crystallizes out, thereby reducing the concentration of the quinine and to some extent nullifying the inhibitive action. On account of this peculiar conduct an experiment with a solution of quinine bisulphate only one-tenth as strong as above is reported here. This is nearly but not quite free from the increasing reaction rate, but still shows a marked inhibitive influence on the part of the quinine, even though its concentration in the solution was only  $\frac{1}{2000}$  molar.

Before.			After.					
T.	V.	$\frac{\Delta V}{\Delta T}$	T.	V.	$\frac{\Delta V}{\Delta T}$	T.	V.	$\frac{\Delta V}{\Delta T}$
0	45.00	...	0	44.00	...	8	40.58	0.42
1	44.19	0.81	1	43.62	0.38	9	40.20	0.38
			2	43.20	0.42	10	39.84	0.36
			3	42.75	0.45	11	39.53	0.31
			4	42.30	0.45	12	39.28	0.25
			5	41.84	0.46	13	39.05	0.23
			6	41.42	0.42	14	38.87	0.18
			7	41.00	0.42			

As is to be seen the inhibitive action of quinine in neutral solution appears to be considerably less than that of brucine. This is possibly due to the influence of the free acid of the acid sulphate since in alkaline solution the quinine seems nearly as powerful as brucine. Following are the results of an experiment in weakly alkaline solution. The solution was made  $\frac{1}{2000}$  molar in quinine.

Before.			After.		
T.	V.	$\frac{\Delta V}{\Delta T}$	T.	V.	$\frac{\Delta V}{\Delta T}$
0	45.00	...	0	43.50	...
1	43.65	1.35	1	43.40	0.10
			2	43.40	0.00
			5	43.40	0.00

That is, in alkaline solution,  $\frac{1}{2000}$  molar quinine is sufficient to practically stop the oxidation of the sodium sulphite. This solution was  $\frac{1}{10}$  normal in potassium hydroxide.

In acid solution quinine conducts itself very much as does brucine.

### c. Experiments with Morphine Hydrochloride.

In this and all following experiments of this group of preliminary investigations, the method of procedure was the same as was used with brucine hydrochloride and with quinine bisulphate. In some cases, where the result in neutral solution was very decisive, the test in alkaline solution was omitted:

#### $\frac{1}{200}$ Molar Morphine Hydrochloride.

Before.			After.		
T.	V.	$\frac{\Delta V}{\Delta T}$			
0	45.00	....	0	43.30	....
1	43.30	1.70	1	42.96	0.34
			2	42.80	0.16
			3	42.65	0.15
			4	42.50	0.15
			5	42.35	0.15
			10	41.68	0.134
			15	41.23	0.092
			45	38.90	0.077



B.			
<i>Before.</i>			
0	45.00	....	
1	43.98	1.02	
<i>After.</i>			
0	44.00	....	
1	43.94	0.06	
2	43.88	0.06	
3	43.82	0.06	
4	43.76	0.06	
5	43.70	0.06	
10	43.42	0.056	
15	43.10	0.060	

*d.*  $\frac{1}{100}$  Molar Atropine Sulphate.

T.	V.	$\frac{\Delta V}{\Delta T}$
<i>Before.</i>		
0	45.00	....
1	42.90	2.10
<i>After.</i>		
0	42.70	....
1	42.25	0.45
2	41.83	0.42
3	41.45	0.38
4	41.10	0.35
5	40.75	0.35
10	39.33	0.284
15	38.30	0.206
20 hrs.	34.40	....
60 hrs.	31.00	....

*e.*  $\frac{1}{100}$  Molar Cane-Sugar.

T.	V.	$\frac{\Delta V}{\Delta T}$
<i>Before.</i>		
0	45.00	....
1	43.35	1.65
<i>After.</i>		
0	43.20	....
1	42.76	0.44
2	42.46	0.30
3	42.20	0.26
4	41.90	0.30
5	41.63	0.27
6	41.38	0.25
7	41.12	0.26
8	40.88	0.24
9	40.66	0.22
10	40.43	0.23

*Added here 1 cc. normal potassium hydroxide.*

0	40.20	....
5	40.20	0.00
10	40.20	0.00
15	40.20	0.00

*f.*  $\frac{1}{100}$  Molar Glycerine.

T.	V.	$\frac{\Delta V}{\Delta T}$
<i>Before.</i>		
0	45.00	....
1	43.10	1.90
<i>After.</i>		
0	42.70	....
1	42.30	0.40
2	42.08	0.22
3	41.86	0.22
4	41.08	0.18
5	41.50	0.18
10	40.60	0.18

*Added here 1 cc. normal potassium hydroxide.*

0	40.48	....
1	40.30	0.18
6	40.30	0.00
11	40.30	0.00
16	40.30	0.00

*g.*  $\frac{1}{100}$  Molar Potassium Cyanide.

T.	V.	$\frac{\Delta V}{\Delta T}$
<i>Before.</i>		
0	45.00	....
1	43.10	1.90
<i>After.</i>		
0	43.00	....
1	42.00	1.00
2	41.53	0.47
3	41.30	0.23
4	41.10	0.20
5	40.90	0.20
6	40.75	0.15
7	40.63	0.12
8	40.50	0.13
9	40.38	0.12
10	40.26	0.12

*Added here 1 cc. normal potassium hydroxide.*

a	40.20	....
1	39.95	0.250
6	39.92	0.006
11	39.82	0.020
16	39.80	0.004
21	39.80	0.000
26	39.80	0.000
31	39.80	0.000

*h.  $\frac{1}{200}$  Molar Ammonium Chloride.*

T.	V.	$\frac{\Delta V}{\Delta T}$
<i>Before.</i>		
0	45.00	....
1	42.55	2.45
<i>After.</i>		
0	42.50	....
1	41.25	1.25
2	39.95	1.30

*Added here 1 cc. normal potassium hydroxide.*

0	39.70	....
1	39.30	0.40
10	39.20	0.022
20	39.10	0.010
30	39.10	0.000
50	39.10	0.000
24 hrs.	39.10	0.000

*i.  $\frac{1}{200}$  Molar Sodium Acetate.*

T.	V.	$\frac{\Delta V}{\Delta T}$
<i>Before.</i>		
0	45.00	....
1	42.90	2.10
<i>After.</i>		
0	42.70	....
1	41.10	1.60

*Added here 1 cc. normal potassium hydroxide.*

0	40.80	....
1	39.25	1.55
2	38.60	0.65
3	38.25	0.35
4	38.00	0.25
5	37.80	0.20
10	37.16	0.13
15	36.78	0.08
20	36.56	0.044

*j.  $\frac{1}{200}$  Molar Pyrogallol.*

T.	V.	$\frac{\Delta V}{\Delta T}$
<i>Before.</i>		
0	45.00	....
1	42.20	2.80
<i>After.</i>		
0	42.00	....
1	41.85	0.15
2	41.83	0.02
3	41.81	0.02
4	41.80	0.01
5	41.78	0.02
10	41.73	0.01
15	41.63	0.02
20	41.56	0.014
25	41.50	0.012

*Added here 1 cc. normal potassium hydroxide.*

T.	V.	$\frac{\Delta V}{\Delta T}$
0	41.50	....
1	39.00	2.50
2	37.20	1.80
3	36.30	0.90
4	36.10	0.20
5	35.93	0.17
10	35.84	0.018
20	35.78	0.006
30	35.76	0.002
40	35.71	0.005
54	35.67	0.004
18 hrs.	33.50	....

In these results for pyrogallol attention is to be called to the very great, but rapidly decreasing, acceleration upon addition of the potassium hydroxide solution. It is, of course, due to the absorption of oxygen by the pyrogallol itself, which takes place

slowly in neutral, but rapidly in alkaline, solution. This phenomenon, however, gives a possible clue to the explanation of all initial accelerations of this sort, and will be treated more in detail in a later paper.

*k. Experiment with  $\frac{1}{100}$  Molar Resorcinol.*

<i>T.</i>	<i>V.</i>	$\frac{\Delta V}{\Delta T}$
<i>Before.</i>		
0	45.00	...
1	42.70	2.30
<i>After.</i>		
0	42.40	...
1	42.10	0.30
2	41.87	0.23
3	41.68	0.19
4	41.48	0.20
5	41.28	0.20

*Added here 1 cc. normal potassium hydroxide.*

0	41.10	...
1	40.80	0.30
6	40.80	0.00
11	40.80	0.00
42 hrs.	40.30	...

*l.  $\frac{1}{100}$  Molar *p*-Oxybenzoic Acid.*

<i>T.</i>	<i>V.</i>	$\frac{\Delta V}{\Delta T}$
<i>Before.</i>		
0	45.00	...
1	43.05	1.95
<i>After.</i>		
0	43.00	...
1	41.70	1.30

*Added here 1 cc. normal potassium hydroxide.*

0	41.60	...
1	40.40	1.20
2	40.33	0.07
3	40.28	0.05
4	40.28	0.00
5	40.28	0.00
2½ hrs.	40.28	0.00

*m.  $\frac{1}{100}$  Molar Hydroxylamine Hydrochloride.*

<i>T.</i>	<i>V.</i>	$\frac{\Delta V}{\Delta T}$
<i>Before.</i>		
0	45.00	...
1	43.70	1.30
<i>After.</i>		
0	43.68	...
5	43.68	0.00
25	43.68	0.00
35	43.68	0.00

*n.  $\frac{1}{100}$  Molar Ethyl Alcohol.*

<i>T.</i>	<i>V.</i>	$\frac{\Delta V}{\Delta T}$
<i>Before.</i>		
0	45.00	...
1	43.80	2.20
<i>After.</i>		
0	42.80	...
1	42.58	0.22
2	42.44	0.14
3	42.30	0.14
4	42.17	0.13
5	42.05	0.12

*Added here 1 cc. normal potassium hydroxide.*

0	42.00	...
1	41.60	0.40
6	41.60	0.00
11	41.60	0.00
24 hrs.	41.55	...

As the preceding studies show, the power to inhibit the oxidation rate of sodium sulphite to a very marked degree belongs to the most diverse organic compounds, as well as to ammonium compounds, hydroxylamine, and potassium cyanide, and in all cases, this power is vastly greater in alkaline than in neutral solution. Further, this inhibitive action is of noticeably different intensity in different cases, although in most cases in alkaline solution, the effect is so great in  $\frac{1}{1000}$  molar solution as to practically totally stop the reaction. In addition to the substances here studied, Bigelow<sup>1</sup> has shown that the power belongs, also, to mannite, succinic and tartaric acids, benzaldehyde, phenol, the three cresols, acetone, several alcohols and aniline. It would thus seem safe to say that this inhibitive action is characteristic to greater or less degree of all organic matter, and in addition, of many nitrogen compounds not organic. That the power belongs distinctly to ordinary distilled water, which contains traces of organic matter and of ammoniacal, or at least proteid, substances is shown very clearly by all attempts that I have made to obtain concordant results with simple water solutions. In such cases, the reaction rate always falls off very markedly toward the end of the reaction. Bigelow also noticed the same phenomenon.

#### 4. EXPERIMENTS TO DETERMINE THE MINIMUM CONCENTRATION OF SEVERAL SUBSTANCES WHICH IS NECESSARY TO PRODUCE MEASURABLE INHIBITION.

In order to determine the minimum concentration of different substances which are capable of producing measurable inhibition a few substances were chosen and each subjected to the following treatment:

(1) A 0.1 molar solution of each substance was prepared and, from this, by successive dilution, were prepared solutions which were respectively 0.01, 0.001, 0.0001, etc., etc., molar.

(2) In each experiment, the normal rate of oxidation of 25 cc. of a solution of 2.5 grams of crystallized sodium sulphite in 200 cc. of distilled water was determined. One cc. of the reagent to be investigated was then added and the rate again measured, the observations being, in general, continued for a considerable time. The concentration of the reagent in the solution is, under these

<sup>1</sup> *Loc. cit.*

conditions,  $\frac{1}{20}$  of that of the reagent added; *i.e.*, by using a 0.001 molar reagent, the solution becomes  $\frac{1}{20,000}$  molar.

(3) Observations were begun in  $\frac{1}{200}$  molar solution and continued with increasing dilution until the reagent failed to produce a noticeable effect.

(4) Each reagent was tested in alkaline and neutral, and sometimes in acid solution. In acid solution, oxygen was used, and in alkaline and neutral solutions, air was used.

The substances investigated in this manner were: Brucine hydrochloride, quinine bisulphate, morphine hydrochloride, cane-sugar and ammonium chloride.

*A. Experiments with Brucine Hydrochloride.*

1. *In Neutral Solution.*—The following tables show the results of several series of measurements with brucine hydrochloride:

TABLE I.— $\frac{1}{200}$  MOLAR BRUCINE HYDROCHLORIDE.

Before.			After.		
T.	V.	$\frac{\Delta V}{\Delta T}$	T.	V.	$\frac{\Delta V}{\Delta T}$
0	50.00	...	0	48.50	...
1	48.50	1.50	1	48.40	0.10
			2	48.30	0.10
			3	48.22	0.08

TABLE II.— $\frac{1}{2000}$  MOLAR BRUCINE HYDROCHLORIDE.

Before.			After.		
T.	V.	$\frac{\Delta V}{\Delta T}$	T.	V.	$\frac{\Delta V}{\Delta T}$
0	50.00	...	0	48.45	...
1	48.50	1.50	1	47.90	0.55
			2	47.35	0.55
			3	46.90	0.45
			4	46.50	0.40
			5	46.10	0.40
			6	45.70	0.40

TABLE III.— $\frac{1}{20,000}$  BRUCINE HYDROCHLORIDE.

Before.			After.		
T.	V.	$\frac{\Delta V}{\Delta T}$	T.	V.	$\frac{\Delta V}{\Delta T}$
0	50.00	...	0	48.20	...
1	48.50	1.50	1	46.90	1.30
			2	45.70	1.20
			3	44.70	1.00
			4	43.80	0.90

TABLE IV.— $\frac{1}{200,000}$  BRUCINE HYDROCHLORIDE.

A.			A.		
Before.			After.		
T.	V.	$\frac{\Delta V}{\Delta T}$	T.	V.	$\frac{\Delta V}{\Delta T}$
0	50.00	...	0	48.30	...
1	48.35	1.65	1	46.65	1.65
			2	45.10	1.55
			3	43.50	1.60
			4	42.00	1.50
B.			B.		
0	50.00	...	0	44.90	...
1	47.50	2.50	1	43.00	1.90
2	45.30	2.20	2	41.60	1.40

As is to be seen from the above tables, the inhibitive action of brucine hydrochloride becomes too small to be detected in neutral solution at a concentration of  $\frac{1}{200,000}$  molar. Even at  $\frac{1}{200,000}$  molar, the initial effect is extremely small if at all present, the values of  $\frac{\Delta V}{\Delta T}$  being so little smaller after than before the addition of the brucine hydrochloride that they are not readily distinguishable from normal values which would naturally decrease, owing to decreasing concentration both of sulphite and oxygen.

It is fairly safe to place the limit of the concentration at which the brucine hydrochloride shows measurable inhibitive effect at somewhere near  $\frac{1}{20,000}$  molar, although, as later results will show, it is probably considerably less than this. In these earlier measurements, the significance of the "development period" was not fully realized.

2. *In Alkaline Solution.*—Preliminary experiments showed that brucine hydrochloride in alkaline solution exerts a vastly greater inhibitive action than in neutral solution. Therefore it is not necessary to give space here to tables of results obtained by using less than  $\frac{1}{20,000}$  molar brucine hydrochloride. As will be seen, the inhibition even at this dilution is practically complete.

TABLE V.— $\frac{1}{20,000}$  BRUCINE HYDROCHLORIDE.

A.			After.		
$\frac{1}{100}$ Potassium Hydroxide.			0	47.70	...
T.	V.	$\frac{\Delta V}{\Delta T}$	1	47.54	0.16
Before.			2	47.50	0.04
0	49.00	...	3	47.47	0.03
1	48.58	0.42	4	47.45	0.02
2	48.18	0.40	5	47.44	0.01
3	47.78	0.40	10	47.40	0.008
			15	47.40	0.000

B.			<i>After.</i>		
<sup>1</sup> / <sub>10</sub> Potassium Hydroxide.			0	43.70	...
<i>T.</i>	<i>V.</i>	$\frac{\Delta V}{\Delta T}$	1	43.60	0.10
			2	43.58	0.02
	<i>Before.</i>		3	43.58	0.00
0	45.00	...	4	43.58	0.00
1	43.80	1.20	5	43.58	0.00

TABLE VI.—<sup>1</sup>/<sub>100,000</sub> BRUCINE HYDROCHLORIDE.

A.			B.		
<sup>1</sup> / <sub>100</sub> Potassium Hydroxide.			<sup>1</sup> / <sub>10</sub> Potassium Hydroxide.		
<i>T.</i>	<i>V.</i>	$\frac{\Delta V}{\Delta T}$	<i>T.</i>	<i>V.</i>	$\frac{\Delta V}{\Delta T}$
	<i>Before.</i>			<i>Before.</i>	
0	49.00	...	0	45.00	...
1	48.20	0.80	1	44.47	0.53
2	47.55	0.65	2	43.93	0.54
3	46.90	0.65	3	43.48	0.45
	<i>After.</i>			<i>After.</i>	
0	46.80	...	0	43.40	...
1	46.34	0.46	1	42.90	0.50
2	46.05	0.29	2	42.50	0.40
3	45.78	0.27	3	42.23	0.27
4	45.54	0.24	4	42.08	0.15
5	45.32	0.22	5	42.00	0.08
6	45.10	0.22	6	41.93	0.07
7	44.90	0.20	7	41.87	0.06
8	44.70	0.20	8	41.83	0.04
9	44.50	0.20	9	41.80	0.03
10	44.30	0.20	10	41.77	0.03
			11	41.75	0.02
			12	41.73	0.02
			13	41.72	0.01
			14	41.71	0.01

TABLE VII.—<sup>1</sup>/<sub>1,000,000</sub> BRUCINE HYDROCHLORIDE.

A.			<i>After.</i>		
<sup>1</sup> / <sub>100</sub> Potassium Hydroxide.			0	42.30	...
<i>T.</i>	<i>V.</i>	$\frac{\Delta V}{\Delta T}$	1	41.73	0.57
	<i>Before.</i>		2	41.30	0.43
0	44.00	...	3	40.90	0.40
1	43.49	0.51	4	40.52	0.38
2	43.00	0.49	5	40.17	0.35
3	42.50	0.50			

B.			<i>After.</i>	
$\frac{1}{10}$ Potassium Hydroxide.				
<i>T.</i>	<i>V.</i>	$\frac{\Delta V}{\Delta T}$		
<i>Before.</i>				
0	45.00	...	0	43.30
1	44.48	0.52	1	42.66
2	43.92	0.56	2	42.05
3	43.40	0.52	3	41.50
			4	41.00
			5	40.53
			10	38.92
			15	38.13
			20	37.58
			21	37.50
				0.64
				0.61
				0.55
				0.50
				0.47
				0.322
				0.158
				0.110
				0.08

An inspection of the above tables shows that in  $\frac{1}{25,000}$  molar solution brucine acts so powerfully as to inhibit practically totally the oxidation of sodium sulphite in alkaline solution. The inhibition is complete in a somewhat shorter time in  $\frac{1}{10}$  normal alkaline solution than in  $\frac{1}{40}$  normal. In  $\frac{1}{25,000}$  molar concentration the inhibition is still very marked, especially in  $\frac{1}{10}$  normal alkaline solution. Here, after a little over 3 cc. of oxygen have been absorbed, the rate has fallen from about 0.5 cc. per minute to 0.01 cc. per minute. In  $\frac{1}{40}$  normal alkaline solution the rate has fallen, after about the same amount of oxygen has been absorbed, to about one-third the original rate. The 25 cc. of the solution used would require for complete oxidation about 13-14 cc. of oxygen (calculated from titration numbers). Thus, neglecting change in concentration of oxygen, as this is relatively insignificant, the fall in the volume absorbed per unit of time under the above conditions should be less than one-fourth. We find with  $\frac{1}{40}$  normal alkali a drop of about two-thirds which distinctly indicates inhibitive action. As to the presence of inhibitive action in 0.1 normal alkaline solution there can be no doubt, as it is very nearly complete.

In  $\frac{1}{25,000,000}$  molar brucine hydrochloride and 0.1 normal potassium hydroxide the rate has fallen, after about one-half has been oxidized, to about one-seventh of the initial rate. Without inhibition it should have fallen to about one-half. In the case of the  $\frac{1}{40}$  normal potassium hydroxide the evidence is not so clear as the experiment was interrupted too soon. One experiment was made with a solution which was  $\frac{1}{25,000,000}$  molar as to brucine hydrochloride. This is here given as Table VIII.



TABLE VIII.

T.	V.	$\frac{\Delta V}{\Delta T}$	T.	V.	$\frac{\Delta V}{\Delta T}$
0	50.00	....	0	48.30	....
1	49.55	0.45	1	47.85	0.45
2	49.15	0.40	2	47.50	0.35
3	48.75	0.40	3	47.18	0.32
4	48.35	0.40	4	46.90	0.28
			5	46.68	0.22
			6	46.45	0.22
			7	46.23	0.21
			8	46.02	0.17
			9	45.85	0.15
			10	45.70	0.17

This, as will be seen, also gives positive evidence of inhibition. But the question arises as to what extent, with ordinary distilled water, inhibition might occur without the addition of brucine and owing solely to some impurity of the water itself or of the salt. To throw some light upon this point a number of observations were made in which no brucine or other substance was added and in which the experiment was continued until about one-half of the sulphite was oxidized. These gave roughly concordant results. One such set is given here:

TABLE IX.

T.	V.	$\frac{\Delta V}{\Delta T}$	T.	V.	$\frac{\Delta V}{\Delta T}$
0	44.00	....	11	38.20	0.32
1	43.20	0.80	12	37.90	0.30
2	42.50	0.70	13	37.62	0.28
3	41.82	0.68	14	37.32	0.30
4	41.24	0.58	15	37.10	0.22
5	40.70	0.54	16	36.88	0.22
6	40.15	0.55	17	36.65	0.23
7	39.70	0.45	18	36.42	0.23
8	39.30	0.40	19	36.26	0.16
9	38.90	0.40	20	36.10	0.16
10	38.52	0.38			

From this it will be seen that after one-half (about 7 cc.) of the requisite amount of oxygen for complete oxidation had been absorbed, the rate had fallen to about one-fourth of the original, thus giving some evidence of inhibition. And it may be added that this inhibition, although not quite so large as with  $\frac{1}{25,000-000}$  brucine hydrochloride, is not with any great degree of certainty to be distinguished from it. Thus it is safe to say that the inhi-

bition by brucine hydrochloride becomes practically indistinguishable from accidental inhibition somewhere between  $\frac{1}{1,000,000}$  and  $\frac{1}{10,000,000}$  molar concentration.

Attention is to be called, in passing, to the development period of the inhibition. With very dilute brucine hydrochloride the rate immediately after adding the reagent is almost as large and sometimes larger than before the addition. The rate then falls off more or less rapidly to a minimum. This, as will be seen later, is a very general phenomenon, and a separate investigation will be devoted to it. Also there is to be noted here the very common occurrence of an initial acceleration upon addition of the brucine hydrochloride. This will also be specially investigated.

3. *In Acid Solution.*—In carrying out the investigation in acid solution a somewhat different method was used. On this account and because the results are of a somewhat different character from the above all studies in acid solution will be brought together under one head at some later time.

#### B. Experiments with Quinine Bisulphate.

1. *In Neutral Solution.*—These experiments, as well as those in alkaline solution, were carried out exactly as were those with brucine hydrochloride.

TABLE X.— $\frac{1}{100}$  MOLAR QUININE BISULPHATE.

T.	V.	$\frac{\Delta V}{\Delta T}$
<i>Before.</i>		
0	45.00	...
1	44.18	0.82
<i>After.</i>		
0	44.10	...
1	43.70	0.40
2	43.22	0.48
3	42.70	0.52
4	42.16	0.54
5	41.62	0.54
6	41.10	0.52
7	40.64	0.46
8	40.18	0.46
9	39.75	0.43
10	39.30	0.45

TABLE XI.— $\frac{1}{1,000}$  MOLAR QUININE BISULPHATE.

T.	V.	$\frac{\Delta V}{\Delta T}$
<i>Before.</i>		
0	45.00	...
1	44.19	0.81
<i>After.</i>		
0	44.00	...
1	43.62	0.38
2	43.20	0.42
3	42.75	0.45
4	42.30	0.45
5	41.84	0.46
10	39.84	0.40
15	38.70	0.23
20	38.15	0.11
30	37.65	0.05
40	37.33	0.023
50	37.15	0.018

TABLE XII.— $\frac{1}{32,000}$  MOLAR QUININE BISULPHATE.

T.	V.	$\frac{\Delta V}{\Delta T}$	<i>After.</i>	
	<i>Before.</i>		0	44.20 ...
			1	43.05 1.15
0	45.00 ...		2	41.75 1.30
1	44.05 0.95		3	40.70 1.05
			4	39.55 1.15
			5	38.25 1.30
			10	34.50 0.75
			15	34.03 0.094
			20	33.94 0.018

TABLE XIII.— $\frac{1}{320,000}$  MOLAR QUININE BISULPHATE.

T.	V.	$\frac{\Delta V}{\Delta T}$
	<i>Before.</i>	
0	45.00 ...	
1	44.20 0.80	
	<i>After.</i>	
0	44.20 ...	
1	43.10 1.10	
2	41.90 1.20	
3	40.83 1.07	
4	39.90 0.93	
5	39.10 0.80	
10	34.35 0.95	
15	33.48 0.18	

TABLE XIV.— $\frac{1}{3,200,000}$  MOLAR QUININE BISULPHATE.

T.	V.	$\frac{\Delta V}{\Delta T}$
	<i>Before.</i>	
0	45.00 ...	
1	44.13 0.87	
	<i>After.</i>	
0	44.10 ...	
1	43.30 0.80	
2	42.48 0.82	
3	41.72 0.76	
4	41.00 0.72	
5	40.28 0.72	
10	36.95 0.666	
15	35.15 0.36	

An examination of these results shows that in dilutions as great as  $\frac{1}{3,200}$  molar, quinine bisulphate shows very distinct inhibitive action. In  $\frac{1}{32,000}$  molar concentration, a distinct initial acceleration is noticed which, however, goes over later into an inhibitive effect. This is more marked when the full set of values per minute is seen, although quite apparent from the abridged table (XII) given here. In Table XIII ( $\frac{1}{320,000}$  molar quinine sulphate), the same acceleration is noticed, while (especially when the table is seen in full) the inhibition is not distinct. In  $\frac{1}{3,200,000}$  molar concentration, the reaction conducts itself as about normal; neither initial acceleration nor inhibition beyond what might be due to the water are apparent. In comparison with brucine hydrochloride, quinine bisulphate acts inhibitive to about the same dilution but shows noticeable initial acceleration, which was not noticed with brucine hydrochloride in neutral solution. The fact that in high concentrations quinine bisulphate does not act so powerfully as brucine hydrochloride, may possibly be

wholly explainable by the formation of the insoluble compound referred to above.

2. *In Alkaline Solution.*—The following tables (XV to XVIII) show the influence of quinine sulphate in alkaline solution. The solutions used were always 0.1 normal in potassium hydroxide.

TABLE XV.— $\frac{1}{2,000}$  MOLAR QUININE BISULPHATE.

T.	V.	$\frac{\Delta V}{\Delta T}$
	<i>Before.</i>	
0	45.00	....
1	43.65	1.35
	<i>After.</i>	
0	43.50	....
1	43.40	0.10
2	43.40	0.00
3	43.40	0.00
4	43.40	0.00

TABLE XVI.— $\frac{1}{20,000}$  MOLAR QUININE BISULPHATE.

T.	V.	$\frac{\Delta V}{\Delta T}$
	<i>Before.</i>	
0	45.00	....
1	43.55	1.45
	<i>After.</i>	
0	43.50	....
1	43.30	0.20
2	43.20	0.10
7	42.90	0.06
12	42.77	0.026

TABLE XVII.— $\frac{1}{200,000}$  MOLAR QUININE BISULPHATE.

T.	V.	$\frac{\Delta V}{\Delta T}$
	<i>Before.</i>	
0	45.00	....
1	44.06	0.94
	<i>After.</i>	
0	43.90	....
1	42.90	1.00
2	42.33	0.57
7	41.17	0.23
12	40.45	0.14

TABLE XVIII.— $\frac{1}{2,000,000}$  MOLAR QUININE BISULPHATE.

T.	V.	$\frac{\Delta V}{\Delta T}$
	<i>Before.</i>	
0	45.00	...
1	43.50	1.50
	<i>After.</i>	
0	44.00	....
1	42.40	1.60
2	41.50	0.90
5	40.08	0.49
10	38.75	0.27
15	38.00	0.15

The result here is wholly comparable to that found for brucine hydrochloride. Out to a dilution of  $\frac{1}{200,000}$  molar the inhibitive action is undoubted. At  $\frac{1}{2,000,000}$  molar, inhibition also seems undoubtedly present and that in much higher degree than that usually shown by solutions in ordinary distilled water without any addition of foreign substances (see Table IX).

### C. Experiments with Morphine Hydrochloride.

Beginning with the morphine hydrochloride the remainder of the measurements given under this section of the work were carried out in a somewhat different manner; namely, the normal rate without addition was first determined, then the foreign sub-

stance injected in the desired quantity and the rate noted, this giving the inhibition in neutral solution, while finally, the further injection of 1 cc. of a normal potassium hydroxide solution and the further determination of the rate gave the result in alkaline solution. All such solutions were thus  $\frac{1}{n}$  normal in potassium hydroxide. The slight change in the concentration of the inhibitive agent may be neglected for present purposes.

This method of procedure has a great advantage over the older one, in point of time saved, while it has the disadvantage of not allowing one to follow the development of the inhibition very far in neutral solution, especially at considerable dilutions, as were this done, the solution would become so far oxidized that the results in alkaline solution might be uncertain. However, as the whole matter of the development period is to be made the subject of special treatment, no particular harm will result.

The following tables (XIX to XXII) give the results with morphine hydrochloride.

TABLE XIX.— $\frac{1}{200}$  MOLAR MORPHINE HYDROCHLORIDE.

T.	V.	$\frac{\Delta V}{\Delta T}$
<i>Before.</i>		
0	45.00	...
1	43.98	1.02
<i>After.</i>		
0	44.00	...
1	43.94	0.06
2	43.88	0.06
3	43.82	0.06
4	43.76	0.06
5	43.70	0.06
10	43.42	0.056
15	43.10	0.060

TABLE XX.— $\frac{1}{1000}$  MOLAR MORPHINE HYDROCHLORIDE.

T.	V.	$\frac{\Delta V}{\Delta T}$
<i>Before.</i>		
0	45.00	...
1	42.60	2.40
<i>After.</i>		
0	42.50	...
1	42.20	0.30
2	41.90	0.30
3	41.62	0.28
4	41.40	0.22
5	41.20	0.20

*Added here 1 cc. normal potassium hydroxide.*

0	41.10	...
1	40.88	0.22
6	40.84	0.008
11	40.80	0.008
16	40.80	0.000

TABLE XXI.— $\frac{1}{10000}$  MOLAR MORPHINE HYDROCHLORIDE.

T.	V.	$\frac{\Delta V}{\Delta T}$
<i>Before.</i>		
0	45.00	...
1	43.70	1.30
<i>After.</i>		
0	43.50	...
1	42.75	0.75
2	42.02	0.73

*Added here 1 cc. normal potassium hydroxide.*

0	42.00	...
1	41.50	0.50
2	41.08	0.42
3	40.80	0.28
4	40.60	0.20
5	40.42	0.18
10	39.96	0.092
15	39.75	0.04
20	39.70	0.01
30	39.70	0.00

TABLE XXII.— $\frac{1}{200,000}$  MOLAR MORPHINE HYDROCHLORIDE.

T.	V.	$\frac{\Delta V}{\Delta T}$
<i>Before.</i>		
0	45.00	...
1	43.15	1.85
<i>After.</i>		
0	43.20	...
1	41.35	1.85

Added here 1 cc. normal potassium hydroxide.

0	41.20	...
1	39.95	1.20
2	39.40	0.55
3	39.15	0.25
4	38.95	0.20
5	38.80	0.15
10	38.36	0.088
15	38.16	0.040
20	38.10	3.010
30	37.88	0.020
40	37.84	0.004
50	37.84	0.000
24 hrs.	37.84	0.000

## D. Experiments with Cane-Sugar.

TABLE XXIII.— $\frac{1}{200}$  MOLAR CANE-SUGAR.

T.	V.	$\frac{\Delta V}{\Delta T}$
<i>Before.</i>		
0	45.00	....
1	43.35	1.65
<i>After.</i>		
0	43.20	....
1	42.76	0.44
2	42.46	0.30
3	42.20	0.26
4	41.90	0.30
5	41.63	0.27
10	40.43	0.24

Added here 1 cc. normal potassium hydroxide.

0	40.20	....
1	40.20	0.00
5	40.20	0.00
10	40.20	0.00
15	40.20	0.00

TABLE XXIV.— $\frac{1}{2000}$  MOLAR CANE-SUGAR.

T.	V.	$\frac{\Delta V}{\Delta T}$
<i>Before.</i>		
0	45.00	....
1	43.00	2.00
<i>After.</i>		
0	43.00	....
1	41.60	1.40

Added here 1 cc. normal potassium hydroxide.

0	41.50	....
1	40.80	0.70
2	40.53	0.27
3	40.38	0.15
4	40.33	0.05
5	40.31	0.02
10	40.20	0.02
15	40.20	0.00

TABLE XXV.— $\frac{1}{20,000}$  MOLAR CANE-SUGAR.

T.	V.	$\frac{\Delta V}{\Delta T}$
<i>Before.</i>		
0	45.00	...
1	42.60	2.40
<i>After.</i>		
0	42.50	...
1	40.70	1.80

Added here 1 cc. normal potassium hydroxide.

0	41.00	...
1	39.30	1.70
2	38.60	0.70
3	38.00	0.60
4	37.60	0.40
5	37.25	0.35
10	36.40	0.16
15	36.08	0.064
20	35.89	0.040
24 hrs.	35.40	...
4 days	35.40	...

TABLE XXVI.— $\frac{1}{200,000}$  MOLAR  
CANE-SUGAR.

T.	V.	$\frac{\Delta V}{\Delta T}$ .
<i>Before.</i>		
0	45.00	...
1	43.00	2.00

*After adding 1 cc. normal potassium hydroxide.<sup>1</sup>*

0	42.50	...
1	41.25	1.25
2	40.45	0.80
3	39.85	0.60
4	39.60	0.25
5	39.35	0.25
6	39.20	0.15
7	39.03	0.17
8	38.93	0.10
9	38.85	0.08
10	38.79	0.06

*E. Experiments with Ammonium Chloride.*TABLE XXVII.— $\frac{1}{200}$  MOLAR AM-  
MONIUM CHLORIDE.

T.	V.	$\frac{\Delta V}{\Delta T}$ .
<i>Before.</i>		
0	45.00	...
1	42.55	2.45
<i>After.</i>		
0	42.50	...
1	41.25	1.25
2	39.95	1.30

*Added here 1 cc. normal potassium hydroxide.*

0	39.70	...
5	39.28	0.084
10	39.20	0.016
15	39.10	0.020
20	39.10	0.000
24 hrs.	39.10	0.000

TABLE XXVIII.— $\frac{1}{2000}$  MOLAR AM-  
MONIUM CHLORIDE.

T.	V.	$\frac{\Delta V}{\Delta T}$ .
<i>Before.</i>		
0	45.00	...
1	42.80	2.20
<i>After.</i>		
0	42.00	...
1	40.60	1.40

*Added here 1 cc. normal potassium hydroxide.*

0	40.30	...
1	39.50	0.80
2	39.35	0.15
3	39.16	0.19
4	39.00	0.16
5	38.85	0.15
10	38.33	0.104
15	38.03	0.060

TABLE XXIX.— $\frac{1}{20,000}$  MOLAR AM-  
MONIUM CHLORIDE.

T.	V.	$\frac{\Delta V}{\Delta T}$ .
<i>Before.</i>		
0	45.00	...
1	43.00	2.00

*After adding 1 cc. normal potassium hydroxide.*

0	42.80	...
1	41.10	1.70
2	40.00	1.10
3	39.30	0.70
4	38.80	0.50
5	38.48	0.32
10	37.10	0.275

The results of the investigations with morphine chloride, cane-sugar and ammonium chloride are thus in a general way wholly comparable with those for quinine and brucine salts. Morphine

<sup>1</sup> In this experiment the potassium hydroxide was added at the same time as the inhibitive reagent. The same is true in Table XXIX.

hydrochloride seems somewhat more active in neutral solution than the other substances. The influence of cane-sugar in alkaline solution seems of about the same value as of the alkaloids, being still very distinct at  $\frac{1}{200,000}$  molar. Ammonium chloride exerts an influence in alkaline solution which rapidly weakens with dilution. Its influence seems to be, in  $\frac{1}{2000}$  molar solution, only about as great as that of morphine hydrochloride in a one hundred times more dilute solution; namely,  $\frac{1}{200,000}$  molar.

#### 5. EXPERIMENTS IN ACID SOLUTIONS.

As has been already stated the study of the oxidation rate of sodium sulphite in acid solution, particularly under the influence of such catalytic accelerators as copper and iron salts is rather complicated. A number of interesting and curious phenomena have been noticed but they have not been sufficiently investigated at present to allow of any report being made. The inhibitive action of organic substances is very much smaller than in neutral solution, and from some observations seems to be zero. In the case of stannous chloride, however, as has been shown,<sup>1</sup> the action in acid solution is very marked. These investigations in acid solution will be carried further.

#### 6. DISCUSSION AND SUMMARY.

In the present incomplete state of this investigation there is no object in entering into any extended discussion of the results. From the results already given, however, certain generalizations are possible.

1. Evidence is shown, tending to lead to the conclusion that only oxidations by means of free oxygen are subject to inhibition by small quantities of foreign substances.

2. A considerable number of organic substances not previously studied by Bigelow<sup>2</sup> show inhibitive action in high degree. In view of the great number of most diverse substances of organic nature which have been shown by Bigelow and by me, to possess this power, it seems safe to conclude that probably all organic substances possess it.

3. In addition to organic substances the power has been shown to belong also to potassium cyanide, hydroxylamine and ammonium salts.

<sup>1</sup> This Journal, 23, 137.

<sup>2</sup> *Loc. cit.*



4. The inhibitive effect has been shown in all cases to be not instantaneous, but to develop somewhat slowly with the oxidation of the solution. Ernst<sup>1</sup> noticed the same phenomenon in studying the influence of foreign substances on the catalytic acceleration of the oxidation of hydrogen by colloidal platinum solution. Bigelow<sup>2</sup> noticed the same depression of the oxidation rate toward the end of the reaction, but ascribed it to other causes.

5. As a very common accompaniment of these phenomena, initial accelerations have been found. It is possible that the method of procedure is alone the cause of these not being observed in all cases.

6. The limit of the dilution at which substances still show inhibitive effects differs for different substances, being in some cases still noticeable at a dilution of  $\frac{1}{1,000,000}$  molar. Investigations are now being carried on whose purpose is to subject these phenomena of development periods and of initial accelerations to a careful study in the hope of finding some simple explanation of them. Until this can be done and the phenomena in question either eliminated or controlled, it is hopeless to attempt any exact quantitative investigation of the subject as a whole.

STANFORD UNIV., CAL.,  
January 9, 1902.

---

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE PENNSYLVANIA STATE COLLEGE.]

## THE ACTION OF METHYL AND ETHYL ALCOHOLS UPON THE BROMIDES OF CERTAIN PROPENYL COMPOUNDS.

BY F. J. POND, E. S. KRB, AND A. G. FORD.

Received December 21, 1901.

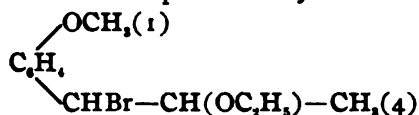
IT has been known for a number of years that certain bromine derivatives of anethol, isosafrol, isoapiol, and other analogous compounds, containing a propenyl group,  $C_3H_5$ , joined to a benzene nucleus, dissolve in ethyl alcohol with apparent decomposition, or on boiling with alcohol, they are converted into compounds which contain a less percentage of bromine. Thus Hell and Günther<sup>3</sup> found that anethol dibromide,  $C_{10}H_{12}O.Br_2$ , is changed into a dark-colored oil on boiling with absolute alcohol; this oil was not prepared in a chemically pure condition, but on

<sup>1</sup> Ernst: *Ztschr. phys. Chem.*, 37, 478

<sup>2</sup> *Loc. cit.*

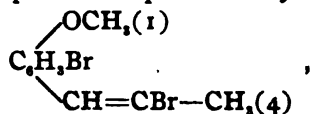
<sup>3</sup> Hell and Günther: *J. prakt. Chem.*, 52, 199.

analysis it gave figures indicating the composition  $C_{11}H_{11}O_2Br$ , and its constitution was represented by the formula



Nothing further appears to have been learned regarding this compound, nor has the action of methyl alcohol on anethol dibromide hitherto been studied.

Also, according to Hell and Günthert,<sup>1</sup> when monobromanethol dibromide,  $C_{10}H_{11}OBr.Br$ , is boiled for some time with absolute ethyl alcohol, ethyl bromide is formed and an oil results which soon solidifies; it separates from ether in crystals melting at  $62^\circ$ . This compound is represented by the formula



and its formation is said to be due to the elimination of 1 molecule of hydrogen bromide from monobromanethol dibromide by means of ethyl alcohol; that is, when anethol dibromide is heated with ethyl alcohol, hydrobromic acid is eliminated and the elements of ethyl alcohol are added, while with the tribromide, hydrogen bromide is given off and an unsaturated bromide,  $C_{10}H_{10}OBr$ , is obtained. The action of methyl alcohol upon the tribromide does not appear to have been investigated.

No definite chemical compounds have been obtained by the action of methyl or ethyl alcohol upon the bromides of other propenyl compounds, although several cases are noted in the literature in which the action of alcohol seems to give rise to non-characteristic oils. For example, Ciamician and Silber<sup>2</sup> found that monobromisafrol dibromide is changed by the action of boiling ethyl alcohol; they refer to this reaction in the following words: "Mit Wasser oder namentlich mit Alkohol gekocht scheint es Bromwasserstoff abzuspalten." Hell and Hoering<sup>3</sup> state that a non-characteristic oil is formed when monobromisafrol dibromide is boiled with ethyl alcohol: "Mit Alkohol erhitzt gaben die Krystalle eine Schmiere, woraus keine Krystalle mehr zu erhalten waren."

<sup>1</sup> Hell and Günthert: *J. prakt. Chem.*, 82, 199.

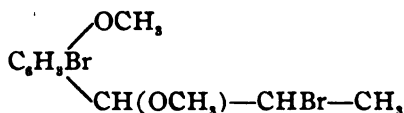
<sup>2</sup> Ciamician and Silber: *Ber. d. chem. Ges.*, 23, 1164.

<sup>3</sup> Hoering: *Inaug. Diss.* (Rostock), p. 59 (1897).

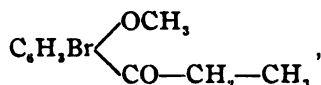
The fact that anisylidene acetophenone dibromide is converted by boiling ethyl alcohol into a definite and crystalline ethyl alcohol addition-product of monobromanisylidene acetophenone,<sup>1</sup> and by methyl alcohol into a corresponding, higher melting methyl alcohol addition-product, led to the belief that similar changes take place when the bromides of certain propenyl compounds are boiled with alcohols. This belief has been justified by the preparation of several characteristic alcohol addition-products.

In our experimental work we have succeeded in preparing the methyl and ethyl alcohol addition-products of monobromanethol by boiling anethol dibromide with the corresponding alcohols. Both compounds are liquids, and are converted into anisyl ethyl ketone,<sup>2</sup>  $C_{10}H_{12}O_2$ , on treatment with *one* molecular proportion of sodium methylate or alcoholic potash; this ketone was first prepared by Wallach and Pond by treating anethol dibromide with *two* molecules of sodium methylate.

It has been found that when monobromanethol dibromide is boiled with, or crystallized from, methyl alcohol, it is converted into the methyl alcohol addition-product,



This substance forms large, magnificent crystals, which melt at  $72^\circ-74^\circ$ . The corresponding ethyl alcohol addition-product is an oil. When these compounds are treated with *one* molecule of sodium alcoholate or alcoholic potash and the resulting product is hydrolyzed with hydrochloric acid, monobromanisyl ethyl ketone,



is obtained. This ketone forms long needles, melts at  $100^\circ$ , and was first prepared by Hell and Hollenberg<sup>3</sup> by the action of *two* molecules of sodium alcoholate upon monobromanethol dibromide.

Two new compounds are obtained by the action of methyl and

<sup>1</sup> Pond and Shoffsall: *This Journal*, **22**, 668 and 670.

<sup>2</sup> Wallach and Pond: *Ber. d. chem. Ges.*, **28**, 2715; see also Hell and Hollenberg: *Ibid.*, **29**, 687.

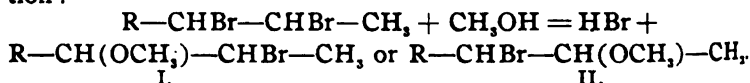
<sup>3</sup> Hell and Hollenberg: *Ber. d. chem. Ges.*, **29**, 686; See Hell and Gärtner: *J. prakt. Chem.*, **51**, 428.

ethyl alcohol on monobromisafrol dibromide,  $C_{10}H_8O_2Br.Br$ ; the methyl alcohol product separates in well-formed crystals, and melts at  $75^{\circ}$ – $76^{\circ}$ , and the ethyl alcohol compound forms large crystals, melting at  $59^{\circ}$ – $60^{\circ}$ . The corresponding monobromoketone,  $C_{10}H_8O_2Br$ , has not been obtained.

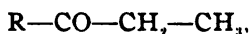
Ethylisoeugenol dibromide,  $C_{12}H_{16}O_2Br_2$ , is also changed by boiling with methyl and ethyl alcohol; the former gives rise to a crystalline compound melting at  $68^{\circ}$ , while the latter yields an oil.

Monobromisoapiol dibromide,  $C_{12}H_{18}O_4Br.Br$ , is converted into a crystalline product on boiling with methyl alcohol; it melts at  $92^{\circ}$ . The ethyl alcohol addition-product is an oil.

The reaction by which these various alcohol addition-products are formed, is probably to be represented by the following equation:



For the present we prefer to represent the alcohol addition-products by the general formula I. This formula more readily explains the formation of ketones,

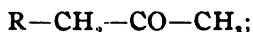


by the action of *one* molecular proportion of sodium alcoholate or alcoholic potash:

1.  $R-CH(OCH_3)-CHBr-CH_3 + KOH =$   
 $R-C(OCH_3)=CH-CH_3 + KBr + H_2O$
2.  $R-C(OCH_3)=CH-CH_3 + H_2O =$   
 $R-C(OH)=CH-CH_3 + CH_3OH$
3.  $R-C(OH)=CH-CH_3 = R-CO-CH_2-CH_3$

It has previously<sup>1</sup> been proved that these ketones contain the carbonyl group in the  $\alpha$ -position to the benzene ring.

If formula II be accepted for these alcohol additive compounds, it would be expected that alcoholic potash would eliminate hydrogen bromide with the ultimate formation of isomeric ketones,



this, however, is not apparently the case.

Owing to the limited time for our work, the investigation of the compounds which are mentioned in the following pages, is

<sup>1</sup> Wallach and Pond: *Ber. d. chem. Ges.*, 28, 2718; see also Hell and Hollenberg: *Ibid.*, 29, 688.

very far from complete, but we deem it desirable to publish the results obtained at this time with the view of reserving this line of research. During the current year we propose to continue these investigations and to extend them to some other propenyl compounds.

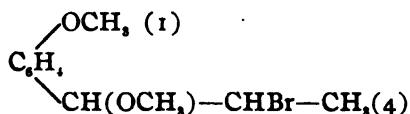
#### EXPERIMENTAL.

*Anethol Dibromide*,  $C_6H_4(OCH_3).C_3H_5Br_2$ , was prepared according to Ladenburg's method.<sup>1</sup>

Forty grams of anethol were dissolved in 200 cc. of ether, and the solution was well cooled with a freezing-mixture; one molecular proportion (43.2 grams) of bromine was added very slowly and with constant shaking. The slight excess of bromine was then removed by shaking the ethereal solution with sulphurous acid, and the ether allowed to evaporate slowly; the resulting crystalline mass was recrystallized from petroleum ether, yielding white needles, which melted at  $62^{\circ}$ – $64^{\circ}$ .

#### *The Action of Methyl Alcohol upon Anethol Dibromide.*

##### *Methyl Alcohol Addition-Product of Monobromanethol,*



A solution of 30 grams of anethol dibromide in 90 cc. of methyl alcohol was boiled for one hour in a reflux apparatus; the solution at first assumed a light pink color, but darkened as the boiling continued. On completion of the reaction the liquid reacted acid, due to the elimination of hydrobromic acid. The contents of the flask were then poured into a large quantity of cold water, and the resulting oil was separated, washed with water and extracted with ether; the ethereal solution was repeatedly shaken with water, dried over anhydrous sodium sulphate, and the ether evaporated. A mobile oil resulted, which had a light yellow color, and was decomposed on distillation. It dissolves readily in alcohol, ether, chloroform and acetic acid, but could not be obtained in a crystalline form. The bromine determination gave:

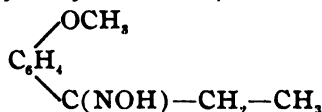
<sup>1</sup> Ladenburg: *Ann. Chem.* (Liebig), Suppl., 8, 94; *Ber. d. chem. Ges.*, 2, 372.

- I. 0.2029 gram gave 0.1456 gram silver bromide.  
 II. 0.2027 gram gave 0.1447 gram silver bromide.

	Calculated for $C_{11}H_{12}O_2Br$	I.	Found.	II.
Bromine.....	30.88	30.54		30.37

When this oil is treated with one molecular proportion of sodium alcoholate and the resulting product is boiled with hydrochloric acid, anisyl ethyl ketone,  $C_{10}H_{12}O_2$ , is obtained.

Forty-four grams of the methyl alcohol addition-product of bromanethol were added to a solution of one molecule of sodium methylate (4 grams of sodium in 100 cc. of methyl alcohol), and boiled for four hours. At the end of this time, the liquid reacted slightly alkaline, and contained considerable sodium bromide. Sufficient water was added to dissolve the sodium bromide and to precipitate the resulting oil. The latter was separated and warmed for about fifteen minutes with dilute hydrochloric acid; it was then distilled with steam. An almost colorless oil was obtained, which, on treatment with hydroxylamine, was converted into a solid oxime. The oxime crystallized from alcohol-ether in large prisms, melting at  $73^{\circ}$ – $74^{\circ}$ ; it is identical in all respects with anisyl ethyl ketoxime,



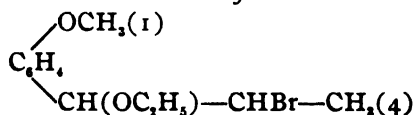
which Wallach and Pond<sup>1</sup> obtained from the oil resulting on the treatment of anethol dibromide with *two* molecules of sodium methylate. On treating this oxime with dilute sulphuric acid, anisyl ethyl ketone (m. p.  $26^{\circ}$ – $27^{\circ}$ ) was formed.

The same oxime (m. p.  $74^{\circ}$ ) was also obtained by a similar treatment of the methyl alcohol addition-product of monobromanethol with one molecule of sodium ethylate and alcoholic potassium hydroxide.

The yield of anisyl ethyl ketone by this method of preparation is better than by the direct action of two molecules of sodium methylate on anethol dibromide.

*The Action of Ethyl Alcohol upon Anethol Dibromide.*

*Ethyl Alcohol Addition-Product of Monobromanethol,*



<sup>1</sup> Wallach and Pond: *Ber. d. chem. Ges.*, 28, 2715.

It was mentioned in the introduction that Hell and Günthert<sup>1</sup> studied this reaction. They found that boiling ethyl alcohol converts anethol dibromide into a dark brown, resinous mass which possesses a strong anethol-like odor; it dissolves in ether, alcohol, benzene, chloroform, and acetic acid. Analysis of this oil gave 28.57 per cent. of bromine, and from this it was regarded that the oil was the ethyl alcohol addition-product of monobrom-anethol,  $C_{12}H_{17}O_2Br$ .

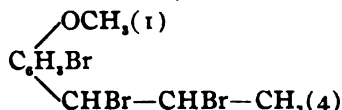
The results of our investigation fully confirm this view. Thirty grams of anethol dibromide were boiled with 90 cc. of ethyl alcohol for one hour, and the reaction-product was poured into cold water. The resulting dark-colored oil was washed repeatedly with water, extracted with ether, again washed, and dried over anhydrous sodium sulphate. On evaporation of the ether, a dark, rather mobile oil resulted; it could not be purified by distillation, but on analysis gave the following results:

- I. 0.2020 gram gave 0.1398 gram silver bromide.  
 II. 0.2028 gram gave 0.1399 gram silver bromide.

	Calculated for $C_{12}H_{17}O_2Br$ .	I.	Found.	II.
Bromine.....	29.30	29.45		29.35

This compound was also readily converted into anisyl ethyl ketone,  $C_{10}H_{12}O$ , by the action of sodium alcoholate or alcoholic potash; its oxime melted at  $72^{\circ}$ – $74^{\circ}$ .

*Monobromanethol Dibromide,*



This compound was first prepared by Cahours<sup>2</sup> by the addition of bromine to anethol; he regarded it as tribromanethol,  $C_{10}H_9Br_3O$ . In 1895, Hell and Gärtner<sup>3</sup> obtained it by adding slowly to a cold, ethereal solution of anethol, the calculated amount of bromine (two molecules). We have found the following method to be the most satisfactory for the preparation of large quantities of the substance.

To a solution of 100 grams of anethol in 75 cc. of ether, 216.2 grams (2 molecules) of bromine are added quite rapidly, the flask

<sup>1</sup> Hell and Günthert: *J. prakt. Chem.*, 52, 199.

<sup>2</sup> Cahours: *Ann. Chem. (Liebig)*, 41, 60.

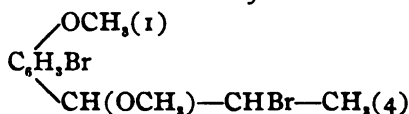
<sup>3</sup> Hell and Gärtner: *J. prakt. Chem.*, 51, 425; 52, 193; see also Orndorff and Morton: *Am. Chem. J.*, 23, 185.

in which the bromination is carried on being placed in ordinary cold water; an especially low temperature and a gradual addition of the bromine are not only unnecessary, but retard the process. When the addition of bromine is complete, the black, oily product is poured into an open dish and allowed to stand, or may be stirred for a few minutes; the product then solidifies with violent evolution of hydrogen bromide. It is now placed on a suction filter, washed very sparingly with ether, and then spread out on a large filter-paper. After twelve hours, it is again washed on a suction filter with a little ether until it assumes a permanent white color. This product melts at  $108^{\circ}$ – $112^{\circ}$ , and is quite pure; it was used in the following described experiments.

Orndorff and Morton<sup>1</sup> purified this compound by dissolving it in a small amount of chloroform and then precipitating with ethyl alcohol. Our experience has been that, although this method gives a pure, crystalline product, a large quantity of the substance suffers decomposition by such treatment, doubtless due to the action of the alcohol.

*The Action of Methyl Alcohol upon Monobromanethol Dibromide.*

*Methyl Alcohol Addition-Product of Dibromanethol,*



—Thirty grams of monobromanethol dibromide were dissolved in 100 cc. of methyl alcohol in a flask fitted with a reflux condenser and boiled for two hours on a steam-bath. The resulting, slightly yellow colored solution had an acid reaction, and gave off fumes of hydrobromic acid; it was poured into a beaker and allowed to stand. In a few hours crystals separated, which were removed and recrystallized from acetone; beautiful, large, colorless prisms resulted, which melted at  $71^{\circ}$ – $74^{\circ}$ .

In another preparation, 135 grams of monobromanethol dibromide were boiled with 380 cc. of methyl alcohol for one hour, the slightly colored solution was filtered and allowed to crystallize. The resultant crystals were repeatedly crystallized from methyl alcohol and finally obtained in large, colorless prisms, melting at  $73^{\circ}$ – $74^{\circ}$ .

It was further learned that the same compound may be readily

<sup>1</sup> Orndorff and Morton: *Am. Chem. J.*, 23, 185.



obtained by dissolving monobromanethol dibromide in methyl alcohol in a beaker, heating the solution to the boiling-point, and allowing to crystallize; on recrystallization from methyl alcohol, the compound is obtained pure and melts at  $73^{\circ}$ – $74^{\circ}$ .

Analyses gave the following results:<sup>1</sup>

- I. 0.2052 gram gave 0.2952 gram carbon dioxide and 0.0816 gram water.
- II. 0.3000 gram gave 0.4308 gram carbon dioxide and 0.1114 gram water.
- III. 0.2128 gram gave 0.2378 gram silver bromide.
- IV. 0.2128 gram gave 0.2380 gram silver bromide.

	Calculated for $C_{11}H_{14}O_2Br_2$	I.	Found. II.	III.	IV.
Carbon.....	39.05	39.23	39.16	....	....
Hydrogen.....	4.14	4.42	4.12	....	....
Bromine.....	47.34	....	....	47.55	47.59

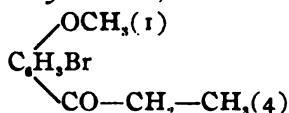
This compound is readily soluble in the usual organic solvents, and may be recrystallized, without change, from boiling ethyl alcohol. On distillation under a pressure of 14 to 15 mm., it boils without decomposition at  $160^{\circ}$ – $164^{\circ}$  yielding a colorless and odorless oil, which solidifies after standing a few hours, and again melts at  $72^{\circ}$ – $74^{\circ}$ ; if the pressure be slightly increased, the compound suffers some decomposition with evolution of hydrogen bromide, and the distillate does not become solid.

When the compound was heated carefully at the atmospheric pressure, it melted to a colorless liquid; at  $130^{\circ}$ , the liquid assumed a yellowish color, which rapidly became darker as the temperature increased. From  $170^{\circ}$ – $195^{\circ}$ , a colorless liquid distilled over and was proved to be methyl alcohol. At  $195^{\circ}$ , the heat was removed, and on cooling, the contents of the flask appeared as a black thick oil, which did not solidify after standing for several months.

It reacts as a saturated compound, since it does not decolorize permanganate and its ethereal solution does not absorb bromine.

An attempt was made to remove the elements of hydrogen bromide by boiling a solution of 20 grams of the compound in 100 cc. of methyl alcohol with 4 grams of anhydrous sodium acetate for twelve hours, but after filtering the reaction-product, the unchanged substance was obtained and melted at  $72^{\circ}$ – $73^{\circ}$ . Hydrobromic acid may be readily removed, however, by the action of sodium alcoholate or alcoholic potash.

<sup>1</sup> These analyses were made by Mr. C. R. Siegfried, to whom we wish here to express our thanks.

*Monobromanisyl Ethyl Ketone,*

—Ten grams of the methyl alcohol addition-product of dibrom-anethol,  $\text{C}_{11}\text{H}_{14}\text{O}_2\text{Br}_2$ , were added to a solution of one molecule of sodium methylate (0.8 gram of sodium in 25 cc. of methyl alcohol), and boiled for two hours. At the end of this time sodium bromide had separated and the liquid reacted slightly alkaline; water was added and the liquid was made slightly acid with hydrochloric acid, when a colorless oil, heavier than water, separated. The aqueous, alcoholic liquid was decanted, and the oil treated with concentrated hydrochloric acid; after stirring for a few seconds, the oil was completely converted into a white solid. The latter was washed free from acid and crystallized from alcohol; it separated in beautiful, long needles, which melted at  $100^\circ-101^\circ$ .

Analyses gave the following results:

- I. 0.3000 gram gave 0.5403 gram carbon dioxide and 0.1364 gram water.  
 II. 0.2008 gram gave 0.1549 gram silver bromide.  
 III. 0.2000 gram gave 0.1549 gram silver bromide.

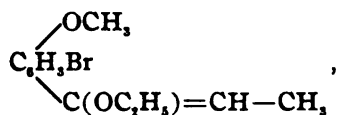
	Calculated for $\text{C}_{10}\text{H}_{11}\text{BrO}_2$	I.	Found. II.	III.
Carbon .....	49.38	49.11	....	....
Hydrogen .....	4.53	5.05	....	....
Bromine .....	32.92	....	32.82	32.95

The formation of this ketone is to be explained by the fact that sodium methylate removes one molecule of hydrogen bromide yielding an unsaturated ether; the latter is hydrolyzed by hydrochloric acid, and the resulting unsaturated alcohol suffers an intramolecular change into the more stable, saturated ketone.

The same ketone (m. p.,  $100^\circ$ ) is also formed by the action of one molecule of potassium hydroxide, dissolved in alcohol, on the methyl alcohol addition-product, and subsequent treatment with hydrochloric acid.

This ketone was prepared by Hell and Hollenberg<sup>1</sup> by the action of two molecules of sodium ethylate upon one molecular proportion of monobromanethol dibromide; they also isolated the unsaturated ether,

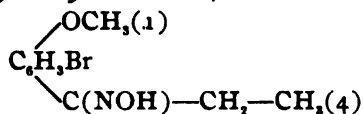
<sup>1</sup> Hell and Hollenberg: *Ber. d. chem. Ges.*, 29, 683; see also Hell and Gärtner: *J. prakt. Chem.*, 81, 424.



which is an oil boiling at  $180^\circ$ – $182^\circ$  (16 mm.), but they did not obtain the first reaction-product, *viz.*, the alcohol addition-product.

To further characterize this ketone, we have converted it into the oxime.

*Monobromanisyl Ethyl Ketoxime,*



—Ten grams of the ketone were dissolved in alcohol and treated in the usual manner with hydroxylamine; on precipitating the reaction-product with water, an oil resulted which soon solidified. It was crystallized from alcohol and separated in splendid crystals, melting at  $108^\circ$ .

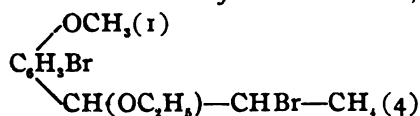
On analysis, it gave the following results for bromine :

- I. 0.2004 gram gave 0.1464 gram silver bromide.  
 II. 0.2003 gram gave 0.1457 gram silver bromide.

	Calculated for $\text{C}_{10}\text{H}_{12}\text{O}_2\text{BrN}$ .	I.	Found.	II.
Bromine .....	31.01	31.08		30.95

*The Action of Ethyl Alcohol upon Monobromanethol Dibromide.*

*Ethyl Alcohol Addition-Product of Dibromanethol,*



A solution of 20 grams of monobromanethol dibromide in 50 cc. of absolute ethyl alcohol was boiled for three minutes on a water-bath; on evaporation of the alcohol, an oil resulted, which was washed with water, extracted with ether, and dried over anhydrous sodium sulphate. After evaporation of the ether over fused calcium chloride in vacuum, a mobile, amber-colored oil was obtained, which gave the following figures on analysis :

- I. 0.2021 gram gave 0.2161 gram silver bromide.  
 II. 0.2012 gram gave 0.2153 gram silver bromide.

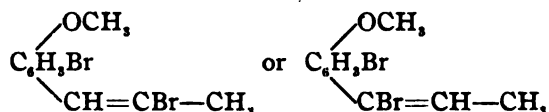
	Calculated for $\text{C}_{12}\text{H}_{16}\text{O}_2\text{Br}_2$ .	I.	Found.	II.
Bromine.....	45.45	45.50		45.53

This compound could not be obtained in a solid condition. The same oil was found in a number of other experiments in which different proportions of alcohol were used, and the boiling was carried on for various lengths of time, from four minutes to three hours.

On heating this oil in a flask to  $196^{\circ}$  under atmospheric pressure, ethyl alcohol is given off and is recognized by the iodoform reaction. The oil does not reduce permanganate in the cold, and its ethereal solution absorbs no bromine.

When this oil is treated with one molecular proportion of sodium alcoholate or alcoholic potash, and then with concentrated hydrochloric acid, it is readily and quantitatively converted into monobromanisyl ethyl ketone, melting at  $99^{\circ}$ – $100^{\circ}$ .

According to Hell and Günthert,<sup>1</sup> when monobromanethol dibromide is boiled with absolute ethyl alcohol for twenty-four hours and the alcohol is then distilled off, ethyl bromide is formed and an oil results which gradually solidifies after pouring into cold water; it crystallizes from ether in long, prismatic crystals which melt at  $62^{\circ}$ . On analysis this compound gave results indicating the formula  $C_{10}H_{10}Br_2O$ , and Hell regards it as an unsaturated bromide,



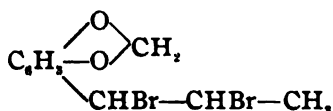
On repeating this experiment, following as closely as possible the directions indicated by Hell, we were unable to obtain the substance in a solid form until the oil had remained for several hours at a temperature below  $0^{\circ}$ . By this method, a small proportion of the oil gradually became solid and, after recrystallization from ether, melted at  $64^{\circ}$ – $66^{\circ}$ ; most of the reaction-product remained as an oil which consisted largely of the ethyl alcohol addition-product above mentioned.

It appears, therefore, that the reaction may take place in two ways, depending on the time that the bromide is heated with the alcohol, and on the subsequent treatment, as the removal of alcohol by gradual evaporation at the ordinary temperature or by distillation; by the former treatment, a product consisting almost entirely of the liquid addition-product results, while the latter

<sup>1</sup> Hell and Günthert: *J. prakt. Chem.*, 82, 199.

method yields some of the solid, unsaturated bromide, together with considerable liquid addition-product.

*Isosafrol Dibromide,*



—The isosafrol necessary for our work was prepared from safrol according to the method of Eykman.<sup>1</sup> It was readily converted into the dibromide<sup>2</sup> by the gradual addition of one molecule of bromine to its cold, ethereal solution. The dibromide remained as a colorless oil after evaporation of the ether.

*The Action of Methyl and Ethyl Alcohols upon Isosafrol Dibromide.*

These reactions were carried on in a manner similar to that mentioned under anethol dibromide by boiling about 50 grams of the dibromide with 150 cc. of the alcohol for one hour. In this case, oils were formed which could not be obtained in a pure condition. Bromine analyses were made of the crude oils, which were purified as carefully as possible. The results are as follows :

1. Oil resulting by boiling isosafrol dibromide with methyl alcohol.

I. 0.2024 gram gave 0.1452 gram silver bromide.

II. 0.2029 gram gave 0.1465 gram silver bromide.

Calculated for		
$\begin{array}{c} \text{C}_6\text{H}_5 \begin{array}{l} \diagup \text{O} \diagdown \\ \diagdown \text{O} \diagup \end{array} \text{CH}_2 \\   \\ \text{CH}(\text{OCH}_3)-\text{CHBr}-\text{CH}_3 \end{array}$		
Bromine.....	29.30	
		Found.
		I.                  II.
		30.52              31.09

2. Oil resulting by boiling isosafrol dibromide with ethyl alcohol.

I. 0.2017 gram gave 0.1388 gram silver bromide.

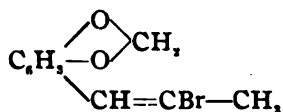
II. 0.2005 gram gave 0.1376 gram silver bromide.

Calculated for.		
$\begin{array}{c} \text{C}_6\text{H}_5 \begin{array}{l} \diagup \text{O} \diagdown \\ \diagdown \text{O} \diagup \end{array} \text{CH}_2 \\   \\ \text{CH}(\text{OC}_2\text{H}_5)-\text{CHBr}-\text{CH}_3 \end{array}$		
Bromine.....	27.87	
		Found.
		I.                  II.
		29.28              29.20

<sup>1</sup> Eykman : *Ber. d. chem. Ges.*, 23, 835; Clamician and Silber : *Ibid.*, 23, 1159; Angeli : *Gazz. chim. ital.*, (2) 23, 101.

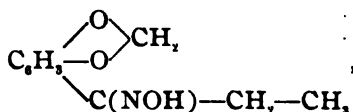
<sup>2</sup> Wallach and Pond : *Ber. d. chem. Ges.*, 28, 2719.

These analyses are, of course, of no value in determining the exact constitution of the two compounds under consideration, but they indicate that the oils are the methyl and ethyl alcohol addition-products of monobromisafrol; for if the action of the alcohols caused the elimination of hydrogen bromide without the addition of the elements of the alcohols, it should give rise, in both cases, to the same compound, monobromisafrol,



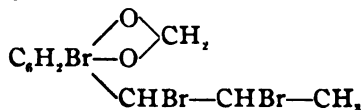
This compound would demand 33.19 per cent. of bromine, which is considerably in excess of that found. In the near future, we hope to obtain these two compounds in a pure condition.

Another circumstance which inclines us to the view that the two oils are alcohol addition-products of monobromisafrol is the behavior of the methyl alcohol product towards sodium alcoholate. When it is boiled with one molecule of sodium alcoholate or alcoholic potash, and the resulting product is treated as usual with hydrochloric acid, a liquid is obtained, which yields an oxime on treatment with hydroxylamine; this oxime crystallizes from alcohol in short prisms, melts at  $101^\circ$ – $102^\circ$ , and is identical with the oxime<sup>1</sup>



which is produced from the compound resulting by the treatment of isosafrol dibromide with two molecules of sodium methylate.

*Monobromisafrol Dibromide,*



—This compound was first prepared by Ciamician and Silber<sup>2</sup> by adding an excess of bromine to a solution of isosafrol in carbon bisulphide, and then heating for a considerable time in a reflux apparatus. It was subsequently obtained by Hell and Hoering<sup>3</sup>

<sup>1</sup> Wallach and Pond: *Ber. d. chem. Ges.*, 28, 2719.

<sup>2</sup> Ciamician and Silber: *Ibid.*, 23, 1163.

<sup>3</sup> Hoering: *Inaug. Diss. (Rostock)*, p. 58, (1897).

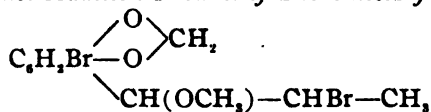
by slowly adding two molecules of bromine to an ethereal solution of isosafrol; the product was recrystallized from petroleum ether, and melted at  $109.5^{\circ}$ .

We find the following method well adapted for the preparation of this compound.

Thirty grams of isosafrol are dissolved in 90 cc. of ether, and 59.3 grams (2 molecules) of bromine are added as rapidly as the reaction will permit, without cooling. The dark-colored reaction-product is allowed to stand in an open vessel until the ether evaporates, when the substance remains as a crystalline mass. It is filtered by suction, washed with a little ether and then with a small quantity of cold alcohol, and crystallized from ethyl acetate; the crystals melt at  $110^{\circ}$ – $111^{\circ}$ . It also crystallizes in large, colorless prisms from a solution in acetone to which an equal volume of ether is added.

*The Action of Methyl Alcohol upon Monobromisafrol Dibromide.*

*Methyl Alcohol Addition-Product of Dibromisafrol,*



—Thirty grams of monobromisafrol dibromide were dissolved in 80 cc. of methyl alcohol and boiled with reflux condenser on the steam-bath for about two hours. The solution became slightly colored and gave an acid reaction; hydrobromic acid was given off. The reaction-product was poured into a beaker and the alcohol allowed to evaporate; the residue consisted of a light-colored, heavy oil, which solidified to a white mass after standing during several days. It was subsequently learned that the same solid compound is more readily formed by boiling the methyl alcoholic solution of the tribromide for about three minutes, and then adding a small quantity of water to the solution; the compound is then precipitated *at once* in fine crystals.

It is recrystallized from methyl alcohol; it separates from a concentrated solution in very fine needles, but from dilute solutions in large, prismatic crystals; both forms of crystals melt at  $75^{\circ}$ – $76.5^{\circ}$ . It may be recrystallized without change from ethyl alcohol.

It was analyzed with the following results:<sup>1</sup>

<sup>1</sup> These analyses were made by Mr. C. R. Siegfried, to whom we wish here to express our thanks.

- I. 0.2118 gram gave 0.2905 gram carbon dioxide and 0.0693 gram water.  
 II. 0.1916 gram gave 0.2634 gram carbon dioxide and 0.0615 gram water.  
 III. 0.2204 gram gave 0.2380 gram silver bromide.  
 IV. 0.2204 gram gave 0.2382 gram silver bromide.

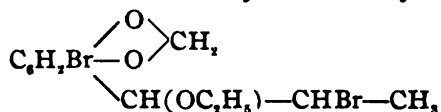
	Calculated for $C_{11}H_{12}O_2Br_2$	I.	Found. II.	III.	IV.
Carbon .....	37.50	37.40	37.49	....	....
Hydrogen.....	3.41	3.63	3.56	....	....
Bromine .....	45.45	....	....	45.94	45.98

Although the corresponding methyl alcohol addition-product of dibromanethol is very readily converted into a ketone by treatment with one molecule of sodium alcoholate or alcoholic potash, no such change appears to take place with this isosafrol derivative. When 10 grams of the compound were heated with an excess of sodium methylate on the steam-bath for twenty-four hours, no reaction took place. The mixture was then heated in an oil-bath at a temperature of  $150^\circ$  until most of the excess of alcohol was removed; no sodium bromide was eliminated and, on the addition of water, an oil separated which soon solidified; this crystallized from alcohol and melted at  $76^\circ$ , indicating the unchanged compound.

Alcoholic potash, and even the action of an excess of metallic sodium on the alcoholic solution of the compound do not remove hydrogen bromide from this substance.

*The Action of Ethyl Alcohol upon Monobromisafrol Dibromide.*

*Ethyl Alcohol Addition-Product of Dibromisafrol,*



—It has already been mentioned that Hell and Hoering<sup>1</sup> have reported on this action; they state that when monobromisafrol dibromide is boiled with alcohol, it yields a non-characteristic oil ("Schmiere") from which no crystalline compound is to be obtained. The results of our experiments do not quite confirm these observations.

When 30 grams of the tribromide were boiled with 80 cc. of absolute ethyl alcohol for about two hours, and the alcohol was then allowed to evaporate, a light-colored, heavy oil separated, which became solid after standing two weeks. It crystallized

<sup>1</sup> Hoering: *Inaug. Diss. (Rostock)*, p. 59, (1897).



from an alcoholic solution in beautiful, large, rhombohedral crystals, and melted at  $58^{\circ}$ – $60^{\circ}$ . The same compound is more readily formed by dissolving the tribromide in ethyl alcohol, heating to the boiling-point for a few minutes, and then adding a small quantity of water; it then separates *at once* in small crystals, which, on recrystallization from alcohol, yield the large crystals above mentioned.

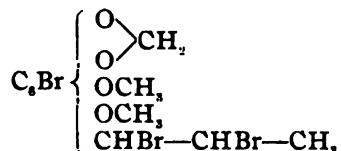
Analysis gave the following:<sup>1</sup>

- I. 0.1835 gram gave 0.2650 gram carbon dioxide and 0.0665 gram water.
- II. 0.1892 gram gave 0.2686 gram carbon dioxide and 0.0658 gram water.
- III. 0.2070 gram gave 0.2130 gram silver bromide.
- IV. 0.2070 gram gave 0.2132 gram silver bromide.

	Calculated for $C_{12}H_{14}O_8Br_2$	I.	II.	Found. III.	IV.
Carbon .....	39.34	39.38	38.71	....	....
Hydrogen .....	3.82	4.02	3.86	....	....
Bromine .....	43.71	....	....	43.78	43.82

When 10 grams of this compound are boiled with an excess of sodium alcoholatè, no action appears to take place, the unchanged substance (m. p.  $58^{\circ}$ – $60^{\circ}$ ) crystallizing from the reaction mixture.

*Monobromisoapiol Dibromide,*<sup>2</sup>



—The isoapiol,<sup>3</sup>  $C_{11}H_{14}O_8$ , necessary for our experiments was prepared by boiling apiol with alcoholic potash; it was recrystallized from acetone and melted at  $55^{\circ}$ – $56^{\circ}$ .

Monobromisoapiol dibromide was first prepared by Ginsberg<sup>4</sup> by the gradual addition of two parts of bromine dissolved in carbon bisulphide to a solution of one part of isoapiol in the same solvent; it was crystallized from glacial acetic acid and melted at  $120^{\circ}$ .

We find that it is more readily prepared by dissolving 52 grams of isoapiol in 52 cc. of ether, and adding 27.5 cc. (2 molecules) of bromine to the solution; the addition of the bromine may take place quite rapidly while the solution is cooled by ordinary cold

<sup>1</sup> These analyses were made by Mr. C. R. Siegfried.

<sup>2</sup> Ginsberg: *Ber. d. chem. Ges.*, 21, 2515.

<sup>3</sup> Ciamician and Silber: *Ber. d. chem. Ges.*, 21, 1621; Ginsberg: *Ibid.*, 21, 1192; See also Gerichten: *Ibid.*, 9, 1479.

<sup>4</sup> *Loc. cit.*

water. The reaction mixture is then placed in a beaker and the ether and hydrogen bromide removed by the aid of a vacuum desiccator. The resulting crystalline mass, which is only slightly colored, is recrystallized from acetone from which it separates in colorless prisms, melting at  $120^{\circ}$ .

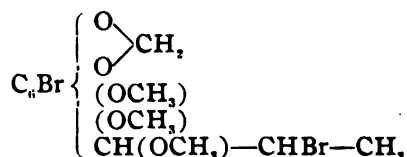
Analyses gave :

- I. 0.3000 gram gave 0.3445 gram carbon dioxide and 0.0772 gram water.  
 II. 0.2000 gram gave 0.2448 gram silver bromide.  
 III. 0.2010 gram gave 0.2451 gram silver bromide.

	Calculated for $C_{12}H_{18}O_4Br_2$	I.	Found. II.	III.
Carbon .....	31.23	31.31	....	....
Hydrogen .....	2.82	2.86	....	....
Bromine .....	52.06	....	52.08	51.88

*The Action of Methyl Alcohol upon Monobromisoapiol Dibromide.*

*Methyl Alcohol Addition-Product of Dibromisoapiol,*



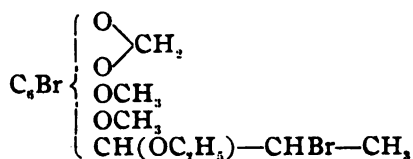
—This compound is formed by boiling monobromisoapiol dibromide with methyl alcohol for about fifteen minutes and then adding a small quantity of water to the hot solution. It usually separates at once in crystals, but under certain conditions it first forms an oil, which rapidly solidifies. It is recrystallized from methyl alcohol and obtained in large prisms, melting at  $92^{\circ}$ .

It was analyzed with the following results :

- I. 0.3001 gram gave 0.4148 gram carbon dioxide and 0.1069 gram water.  
 II. 0.3006 gram gave 0.4143 gram carbon dioxide and 0.1092 gram water.  
 III. 0.2006 gram gave 0.1828 gram silver bromide.  
 IV. 0.2013 gram gave 0.1838 gram silver bromide.

	Calculated for $C_{12}H_{16}O_4Br_2$	I.	Found. II.	III.	IV.
Carbon .....	37.86	37.69	37.58	....	....
Hydrogen .....	3.88	3.95	4.03	....	....
Bromine .....	38.83	....	....	38.78	38.85

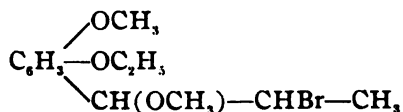
Sodium alcoholate is apparently without action upon this compound.

*The Action of Ethyl Alcohol upon Monobromisoapiol Dibromide.**Ethyl Alcohol Addition-Product of Dibromisoapiol,*

—Monobromisoapiol dibromide was boiled with three times its quantity of ethyl alcohol for about forty-five minutes. The solution had a dark color and an acid reaction; on the addition of water, an oil separated, which was carefully washed with water, extracted with ether and dried. On evaporation of the ether a rather dark-colored, viscous oil resulted, which gave the following results on analysis for bromine:

- I. 0.2077 gram gave 0.1835 gram silver bromide.  
 II. 0.2137 gram gave 0.1840 gram silver bromide.

	Calculated for $\text{C}_{14}\text{H}_{18}\text{O}_2\text{Br}_2$	I.	Found.	II.
Bromine .....	37.56	36.98		36.63

*The Action of Methyl Alcohol upon Ethylisoeugenol Dibromide.**Methyl Alcohol Addition-Product of Ethylmonobromisoeugenol,*

—Forty grams of ethylisoeugenol dibromide,<sup>1</sup>  $\text{C}_{12}\text{H}_{16}\text{O}_2\cdot\text{Br}_2$ , were boiled with 100 cc. of methyl alcohol for about two hours, and the reaction-product allowed to stand in an open dish until the excess of alcohol evaporated. The residue consisted of an oil which gradually solidified; this was filtered by suction, washed sparingly with cold alcohol, and repeatedly crystallized from ethyl alcohol. It was rather difficult to remove some oily impurities from the compound, but after boiling with animal charcoal, it crystallized from alcohol in large colorless prisms, melting at  $68^\circ$ . It is quite soluble in methyl and ethyl alcohols, ether and acetone.

<sup>1</sup> Wallach and Pond: *Ber. d. chem. Ges.*, 28, 2720.

Analysis gave the following :

- I. 0.2009 gram gave 0.1243 gram silver bromide.  
 II. 0.2008 gram gave 0.1237 gram silver bromide.

	Calculated for $C_{12}H_{16}O_2Br$ .	I.	Found.	II.
Bromine.....	26.40	26.32		26.21

It should also be mentioned that in one preparation of this compound by boiling ethylisoeugenol dibromide with methyl alcohol, another compound was formed, together with the methyl alcohol addition-product ; it was separated by fractional crystallization from ethyl alcohol in which it is more sparingly soluble than the addition-product. It crystallizes in fine needles and melts at  $128^{\circ}$  ; it contains no bromine, but has not been further investigated.

[CONTRIBUTION FROM THE NORTH CAROLINA AGRICULTURAL EXPERIMENT STATION. COMMUNICATED BY W. A. WITHERS.]

### THE DETERMINATION OF SULPHUR IN PLANTS.

By G. S. FRAPS.

Received December 5, 1901.

IN a previous issue of this Journal<sup>1</sup> the author called attention to the loss of sulphur in preparing ash of plants. The conclusion reached was that "the sulphur obtained when the ash was burned by itself is from 4 to 100 per cent. less than when burned with calcium acetate. Whether the calcium acetate retains all the sulphur or not, is a point which requires further study." The facts which will be presented here show that the calcium acetate does not retain all the sulphur.

The object of the work was to compare the calcium acetate method with some method by the use of which we could be reasonably certain that all the sulphur contained in the plant in inorganic or organic combination would be retained and determined. A great difficulty is that a very small amount of sulphur is contained in a large quantity of plant material. The Liebig method (fusion with potassium hydroxide and a small amount of potassium nitrate in a silver dish) and the Carius method (heating in a sealed tube with fuming nitric acid) were considered, but offered difficulties on account of the large quantity of organic material to be handled. The following method was finally adopted for trial:

Fifteen grams material were placed in a flat porcelain dish of about 250 cc. capacity, 35 cc. of nitric acid (conc.) added, and the

<sup>1</sup> 23, 199 (1901).

mixture heated gently until the action had moderated. One gram potassium nitrate was then added, and the mixture evaporated to a thin paste, transferred to a platinum dish, evaporated on a water-bath, and ignited to an ash. After heating for some time, the ash was dissolved in dilute hydrochloric acid, the solution evaporated to dryness, and the residue dried thoroughly to render silica insoluble. It was moistened with a little dilute hydrochloric acid, evaporated, and again dried. The residue was moistened with about 5 cc. of hydrochloric acid, taken up with about 50 cc. of boiling water, filtered, and sulphuric acid determined in the filtrate by the usual method.

A blank determination with the reagents proved them to be free from sulphur. The sulphur (as sulphur trioxide) found by this method compared with the others is given in the following table :

SULPHUR TRIOXIDE IN PLANT (AIR-DRY).

	In ash (usual way). Per cent.	In calcium acetate ash. Per cent.	Nitric acid method. Per cent.
Wheat bran .....	...	0.221	0.368
Cottonseed meal .....	...	0.343	0.926
Green rape .....	1.02	1.25	1.63
Wheat bran .....	0.00	0.14	0.30
Corn silage.....	0.20	0.24	0.43
Timothy hay .....	0.15	0.17	0.28

It is evident that the calcium acetate method does not give correct values for sulphur.

It is not believed that the loss of sulphur is due to volatilization of *sulphates*, but to the escape of organic sulphur compounds which are not burned or oxidized. Most of the sulphur in a plant is not in the form of sulphates, but is in an organic form, and it is not surprising that it is lost under the conditions. The same would be true of *chlorine*, which is probably much more difficult to retain than sulphur.

The following modification of the nitric acid method just described has been found more convenient. It calls for the use of a smaller quantity of material, and leaves out the platinum dish, which is liable to be damaged under certain conditions.

Five grams material are placed in a 3½ inch porcelain evaporating dish, 20 cc. of concentrated nitric acid added, and the mixture heated cautiously on the water-bath until all danger of overflowing has passed. It is then partly evaporated, 10 cc. of a

5. per cent. solution of potassium nitrate added, the mixture evaporated to dryness and ignited, at first gently, then under a blast-lamp, until the residue is white. It is then dissolved in hydrochloric acid, evaporated to dryness, and heated for some time in an air-bath to render silica insoluble. The residue is taken up in water with the addition of a little acid, filtered, and the sulphuric acid precipitated with barium chloride, etc., in the usual way.

---

[CONTRIBUTION FROM THE HAVEMEYER LABORATORIES OF COLUMBIA UNIVERSITY, No. 61].

### ON THE RELATION OF THE HEAT OF COMBUSTION TO THE SPECIFIC GRAVITY IN FATTY OILS.

By H. C. SHERMAN AND J. F. SNELL.

Received January 4, 1900.

FROM data given in a previous paper<sup>1</sup> it was inferred that among the common fatty oils there exists a certain definite relation between the heat of combustion and the specific gravity. Thus, comparing such typical oils as those of linseed, poppyseed, maize, cottonseed, sesame, almond, and olive, we find that the decrease in drying properties is accompanied by a decrease in specific gravity and a nearly proportional increase in the calorific power, so that the product of these two values shows comparatively little variation. It also seemed probable from the examination of a few samples which were known to have been oxidized by exposure, that such oxidation reduces the heat of combustion to nearly the same extent that it increases the specific gravity. We are now able to give additional data in support of each of these inferences.

The determinations of specific gravity and of heat of combustion have been made by the methods described in our previous paper and we are again indebted to Professor Atwater, for the privilege of doing a considerable part of the work in the laboratories of Wesleyan University. The heats of combustion given in the tables below are those obtained at constant volume; *i. e.*, the results actually shown by the calorimeter. The corresponding values for combustion at constant pressure may be calculated as already explained.<sup>2</sup>

Table A shows the specific gravities and heats of combustion

<sup>1</sup> This Journal, 23, 164.

<sup>2</sup> *Ibid.*, 23, 167.

of the fatty oils thus far examined which were either fresh or had been well protected from the air, so that no considerable oxidation is believed to have taken place. The last two columns give respectively the product obtained by multiplying, and the quotient obtained by dividing the heat of combustion (in large calories per gram) by the specific gravity. A few non-fatty oils are added at the end of the table.

TABLE A.—RELATION OF SPECIFIC GRAVITY TO HEAT OF COMBUSTION IN FATTY OILS WHEN FRESH.

Lab. No.	Variety of oil:	Sp. gr. 15.5° 15.5°	Calories per gram.	Calories × sp. gr.	Calories ÷ sp. gr.
2052	Raw linseed, I .....	0.934	9.364	8.74	10.03
2070	Raw linseed, II .....	0.938	9.379	8.80	10.00
2122	Raw linseed, IV .....	0.933	9.381	8.75	10.05
Aver.	Raw linseeds .....	0.935	9.375	8.77	10.03
2073	Boiled linseed, I .....	0.934	9.394	8.77	10.06
2127	Boiled linseed, II .....	0.935	9.349	8.74	10.00
Aver.	Boiled linseeds <sup>1</sup> .....	0.935	9.372	8.76	10.02
2069	Poppyseed .....	0.926	9.382	8.69	10.13
2056	Maize oil, I .....	0.924	9.413	8.71	10.19
2066	Maize oil, II .....	0.926	9.436	8.74	10.19
2092	Maize oil, III (dark) .....	0.926	9.419	8.72	10.17
Aver.	Maize oils .....	0.925	9.423	8.72	10.19
2063	Sesame .....	0.924	9.395	8.68	10.17
2053	Cottonseed, I .....	0.920	9.396	8.64	10.21
2054	Cottonseed, II .....	0.921	9.401	8.66	10.21
2055	Cottonseed, III .....	0.923	9.390	8.67	10.17
2089	Cottonseed, IV (dark) ....	0.927	9.397	8.71	10.14
Aver.	Cottonseed oils .....	0.923	9.396	8.67	10.18
2102	Rape, I .....	0.920	9.489	8.73	10.31
2065	Rape, II .....	0.920	9.462	8.71	10.29
Aver.	Rape oils .....	0.920	9.476	8.72	10.30
2061	Peanut (arachis) .....	0.917	9.412	8.63	10.26
2064	Almond .....	0.919	9.454	8.69	10.29
2058	Olive, I .....	0.917	9.457	8.67	10.31
2093	Olive, II .....	0.916	9.451	8.66	10.32
Aver.	Olive oils .....	0.917	9.454	8.67	10.31
2091	Castor .....	0.967	8.863	8.57	9.17
2062	Castor .....	0.964	8.835	8.52	9.16
Aver.	Castor oils .....	0.966	8.849	8.55	9.16
2076	Menhaden .....	0.935	9.360	8.75	10.01

<sup>1</sup> Only boiled linseed oils of low specific gravity are here included. Data of other samples are given in Table B. It was recently found that the figures given for boiled linseed oil in our previous paper were incorrect. Through an error the heat of combustion was determined on a sample different from that in which determinations of specific gravity, iodine absorption, and acidity had been made.

Lab. No.	Variety of oil.	Sp. gr. $\frac{15.5}{15.5}$	Calories per gram.	Calories $\times$ sp. gr.	Calories $+$ sp. gr.
2077	Menhaden.....	0.934	9.371	8.76	10.03
Aver.	Menhaden oils.....	0.935	9.366	8.76	10.02
2104	Cod-liver .....	0.926	9.434	8.74	10.19
1998	Cod-liver .....	0.927	9.437	8.75	10.18
Aver.	Cod-liver oils .....	0.927	9.436	8.75	10.18
2103	Seal oil.....	0.926	9.424	8.73	10.18
2084	Whale oil.....	0.924	9.473	8.75	10.25
2057	Lard oil, I.....	0.917	9.451	8.67	10.31
2060	Lard oil, II.....	0.919	9.447	8.68	10.28
Aver.	Lard oils .....	0.918	9.449	8.67	10.29
2080	Sperm oil.....	0.886	9.946	8.81	11.23
2081	Rosin oil .....	0.989	10.145	10.03	10.76
2098	Petroleum oil, I.....	0.881	10.797	9.51	12.26
2099	Petroleum oil, II.....	0.897	10.753	9.64	11.99
2100	Petroleum oil, III.....	0.905	10.682	9.67	11.80
Aver.	Petroleum oils .....	0.894	10.744	9.61	12.01
2143	Turpentine .....	0.862	10.800	9.31	12.52

Excepting the castor oils, which, of course, differ from all the others in containing a large proportion of ricinolein, the value obtained by multiplying the heat of combustion by the specific gravity shows very little variation as between oils of the same variety, while as between the different classes of oils this value decreases with the specific gravity, but to a less degree. The value obtained by dividing the heat of combustion by the specific gravity varies, of course, in the opposite direction and to a greater degree. Thus the difference between these two values increases as we pass from the oils of higher to those of lower specific gravity. These relations hold as well for the fatty oils of animal as for those of vegetable origin. The non-fatty oils, on the other hand, show quite different relations.

Table B shows the results obtained upon a number of commercial oils which had specific gravities higher than the corresponding fresh oils and which are believed to have been more or less oxidized by exposure to the air. In nearly all cases such exposure is known to have occurred. A sample of blown rapeseed oil is also included.



TABLE B.—RELATION OF SPECIFIC GRAVITY TO HEAT OF COMBUSTION IN "EXPOSED" FATTY OILS.

Lab. No.	Variety of oil.	Sp. gr. $\frac{15.5^\circ}{15.5^\circ}$	Calories per gram.	Calories $\times$ sp. gr.	Calories $\div$ sp. gr.
2082	Raw linseed, III.....	0.947	9.215	8.73	9.73
2123	Raw linseed, V.....	0.941	9.274	8.73	9.86
2124	Raw linseed, VI.....	0.952	9.099	8.66	9.56
Aver.	Raw linseeds.....	0.947	9.196	8.71	...
2072	Boiled linseed, III.....	0.949	9.191	8.72	9.69
2125	Boiled linseed, IV.....	0.951	9.152	8.70	9.62
2126	Boiled linseed, V.....	0.944	9.275	8.76	9.83
Aver.	Boiled linseeds.....	0.948	9.206	8.73	...
1999	Cottonseed, V (dark).....	0.927	9.336	8.65	10.07
2087	Cottonseed, VI.....	0.929	9.323	8.66	10.04
2067	Cottonseed, VII (old).....	0.941	9.168	8.63	9.74
Aver.	Cottonseed oils.....	0.932	9.276	8.65	...
2086	Rapeseed.....	0.926	9.412	8.72	10.16
2111	Blown rapeseed.....	0.974	8.805	8.58	9.04
2094	Almond.....	0.931	9.311	8.67	10.00
2085	Cod-liver.....	0.938	9.277	8.70	9.89
2059	Lard oil, III.....	0.924	9.372	8.66	10.14
2095	Lard oil, IV.....	0.922	9.394	8.66	10.19
Aver.	Lard oils.....	0.923	9.383	8.66	....

In this table the figures in the last column are, of course, lower than the corresponding figures in Table A and are quite variable, being dependent upon the extent to which the samples had become oxidized. The values obtained by multiplying the heat of combustion by the specific gravity are very little different from the corresponding values in Table A; in other words, the effect of exposure was to cause an increase in specific gravity and a nearly equal decrease in heat of combustion.

In general the oils which had been exposed showed slightly more free acid than those in Table A. Hydrolysis of fat with liberation of fatty acid involves an absorption of water. To split off 1 per cent. of oleic acid, about 0.06 per cent. of moisture must be taken up. The oils examined contained very little free acid and for our purpose it is probably safe to neglect the small amounts of water involved. It may be noted, however, that any moisture thus taken up would lower the heat of combustion more than it would raise the specific gravity, thus decreasing the value of the product of these two factors; and it will be seen that such slight discrepancies as are found by a comparison of Tables A and B are always in this direction.

Sample No. 2067, an old cottonseed oil, shows such remarkable results that (as the history of the sample was not known) it seemed advisable to determine the elementary composition, in order to confirm the assumption that its peculiar properties were due to oxidation. It yielded, on analysis,

	Per cent.
Carbon .....	73.66
Hydrogen .....	11.34
Oxygen .....	15.00

Sample No. 2054, which was known to be fresh and was selected as being typical, yielded

	Per cent.
Carbon .....	76.65
Hydrogen .....	11.74
Oxygen .....	11.61

The increased percentage of oxygen found in the older sample is quite sufficient to account for the observed differences in specific gravity and heat of combustion; and while the elementary analyses are not in exact proportion to these differences, the agreement is perhaps as close as could be expected between samples produced by different methods at an interval of several years.<sup>1</sup>

Conclusions drawn from a comparison of the figures given in Table B, with those in Table A are open to objection inasmuch as the samples of "fresh" and of "exposed" oils of a given variety are not always from the same source, though the fact that the relations noted apply to each of the seven varieties included in the comparison makes it improbable that they are accidental.

In raw and boiled linseed oils, however, we have obtained sufficient oxidation by exposure in uncorked bottles for two to four months, to give positive confirmation of the inferences already drawn. Thus sample No. 2052, raw linseed oil, and sample No. 2072, boiled linseed oil, gave the following :

<sup>1</sup> A similar comparison was attempted in the case of the blown rape oil (No. 2111), No. 2102 being selected as a typical fresh sample for comparison. The latter yielded : Carbon, 76.23 per cent.; hydrogen, 11.52 per cent.; oxygen, 12.25 per cent. The blown oil yielded figures for carbon ranging from 71.22 to 73.00 per cent., and for hydrogen from 10.61 to 11.09 per cent. This would indicate that the extremely high viscosity of the sample prevented thorough mixing, in which case the determination of heat of combustion may also be less accurate than in the other samples. In general terms, however, it may be said that the increased percentage of oxygen in the blown oil corresponds approximately to the increase in specific gravity and decrease in heat of combustion.

	Sp. gr. at 15.5°.	Calories per gram.	Calories X sp. gr.
Raw linseed before exposure .....	0.934	9.364	8.74
Same after four months' exposure ...	0.942	9.288	8.75
Boiled linseed before exposure.....	0.949	9.191	8.72
Same after two months' exposure....	0.9595	9.078	8.71
Same after four months' exposure ...	0.968	8.963	8.68

The boiled linseed oil after four months' exposure was so thick that the determinations made upon it may be less accurate than in the other cases. Elementary analyses were made of the boiled linseed oil, before and after the two months' exposure, with the following results :

	Carbon.	Hydrogen.	Oxygen.
Before exposure .....	75.02	10.73	14.25
After exposure.....	74.15	10.70	15.15

Here the exposure, while raising the specific gravity 1.1 per cent. and lowering the heat of combustion 1.2 per cent., has lowered the combined percentages of carbon and hydrogen 1.1 per cent. of the amount originally present.

The simplest interpretation of these relations would be that the oil took up from the air an amount of oxygen equal to 1.1 per cent. of its original weight and that this oxygen was absorbed without appreciable increase of volume or loss of carbon or hydrogen. It seems probable also that each of the oils shown in Table B above had absorbed oxygen in the same manner.

A study of the quantitative relations of the changes produced by such oxidation in the usually determined "constants" is being carried on in this laboratory, and it is hoped that this may lead to more definite knowledge of the significance of these constants.

We believe that the data here given justify the following conclusions :

1. In fresh fatty oils the heat of combustion is a property quite as constant as the specific gravity, to which it bears a certain definite relation.
2. Oxidation resulting from exposure to air decreases the heat of combustion to practically the same extent that it increases the specific gravity. Hence it is to be inferred that the oxygen is taken up by direct addition and without essential change in the volume of the oil.
3. On account of its close quantitative relations to the specific gravity and ultimate composition, the heat of combustion is likely to prove a useful factor in the further study of the fatty oils.

## ACTION OF SELENIC ACID ON GOLD.<sup>1</sup>

BY VICTOR LENHER.

Received January 6, 1902.

**I**N a number of text-books and works of reference on chemistry, it is stated that gold is attacked by hot selenic acid, the latter being reduced. The details of the reaction do not seem to have been worked out, nor the products investigated.

The statement that gold is dissolved by selenic acid finds its origin in the work of Mitscherlich,<sup>2</sup> who was the first to prepare and study the properties of selenic acid. He states that selenic acid dissolves gold but not platinum.

Inasmuch as selenic acid in presence of hydrochloric or hydrobromic acid is reduced to selenious acid with the liberation of halogen, which would act on gold, and since no selenate of gold appears to be described in the literature, it seemed well to investigate this reaction and ascertain whether gold would dissolve in pure selenic acid which contained no halogen, and if solution actually took place, what the products of the reaction would be.

In order to preclude the possibility of the presence of a halogen in the selenic acid used, the acid was prepared as follows: Resublimed selenium dioxide was fused with pure potassium nitrate. The resulting selenate was dissolved in water and to a dilute solution, a solution of lead nitrate was added; the resulting precipitate of lead selenate was repeatedly washed with water until pure. It was then suspended in water and treated with hydrogen sulphide gas. Lead sulphide was obtained along with any selenium existing as selenite. The dilute selenic acid which resulted was concentrated on the water-bath and was used in the following work. For a preparation of a part of the selenic acid used, the author is indebted to Mr. W. H. Richardson.

The fairly concentrated acid which was thus obtained was brought into contact with gold leaf. No action was apparent in the cold. By evaporation, it is possible to concentrate selenic acid, and when the acid is hot and concentrated, gold dissolves readily to a reddish yellow solution. The action begins at about 230°, but proceeds much more readily at about 300°; selenium dioxide is evolved, while the gold goes into solution as auric sele-

<sup>1</sup> Read at the Philadelphia meeting of the American Chemical Society.

<sup>2</sup> Pogg. Ann., 12, 630.

nate,  $\text{Au}_2(\text{SeO}_4)_3$ . Analysis of the salt showed that it agrees with this formula. The gold leaf was replaced by small pieces of gold, and it was found that the latter dissolve nearly as readily as the leaf and at about the same temperature. In most respects the action is similar to that of sulphuric acid on copper, although no such complicated products arise as mentioned by Baskerville<sup>1</sup> in the study of this reaction.

The selenate has been obtained as very small yellow crystals. It is soluble in hot concentrated selenic acid, forming a reddish-yellow solution, and separates on cooling. It is insoluble in water, and can be completely separated from selenic acid by dilution, when it appears as a yellow precipitate. It is soluble in sulphuric acid and in nitric acid. Hydrochloric acid decomposes the salt with evolution of chlorine, forming auric chloride and selenious acid. It is decomposed by heat below redness, metallic gold being obtained. On exposure to the light, auric selenate is decomposed, becoming dark green then bronze colored. It is worthy of note that all the members of the subgroup B in the first group of the periodic system, dissolve in selenic acid with evolution of selenium dioxide and formation of the corresponding selenate. Silver dissolves in selenic acid when the latter is hot and concentrated, the selenate being produced and selenium dioxide being evolved. Copper also acts in a similar manner. During the solution of gold in selenic acid, selenium dioxide is produced, being evolved as fumes, and is also invariably found in the solution after the reaction. Moreover in the reaction of selenic acid on gold we have for the first time the solution of gold in a simple oxygen acid.

UNIVERSITY OF WISCONSIN,  
MADISON, WIS.

### NATURALLY OCCURRING TELLURIDE OF GOLD.<sup>2</sup>

BY VICTOR LENHER.

Received January 6, 1902.

THE occurrence of gold in nature, according to the commonly accepted view, is either as native gold or as telluride. It is generally conceded that gold exists in pyrite or other sulphide ores uncombined and in the elementary condition. This, broadly speaking, is the manner in which gold is considered to exist in nature. No mineral containing gold as one of its constituents,

<sup>1</sup> Baskerville: This Journal, 17, 904.

<sup>2</sup> Read at the Philadelphia meeting of the American Chemical Society.

and no chemical compound of gold is known in nature with the possible exception of the so-called "tellurides" or the tellurides of gold.

It is the purpose of this paper to describe a series of experiments which have been conducted with the view of throwing some light on the constitution of the naturally occurring tellurides.

The peculiar combinations of gold and tellurium which occur in nature have a more or less definite and more or less indefinite character, both from the standpoint of the chemical mineralogist and of the crystallographer. The recorded analyses of the telluride minerals show considerable variation from a constant composition.

One of the best defined compounds of gold and tellurium occurring in nature, and the compound which contains the nearest to pure tellurium and gold has been called "calaverite."

Calaverite is a silver-white mineral, frequently possessing striated faces, containing in composition from 55.8 to 57.6 per cent. tellurium, 40.6 to 42.7 per cent. gold, and smaller quantities of silver, 0.40 to 3.0 per cent. The theoretical requirements for  $\text{AuTe}$ , are 56.32 per cent. tellurium and 43.68 per cent. gold. This mineral contains more gold and less silver than the other tellurides. This combination of gold and tellurium appears to present some definite characteristics of a mineral. The recent work of Penfield and Ford<sup>1</sup> seems to throw some doubt on the definiteness of its crystallographic constants. In this valuable paper, measurements of crystal faces are given, which show either monoclinic or triclinic symmetry.

Sylvanite, one of the most common tellurides of Colorado and West Australia, occurs in brilliant white twinned crystals which are frequently distributed over the faces of rocks in such a manner as to resemble Arabic writings; hence, it has been called "graphic tellurium." This mineral contains about 60 per cent. tellurium, 16 per cent. gold, and 14 per cent. silver. Other tellurides, which are well defined, are krennerite and petzite.

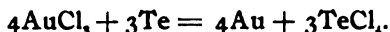
Finally, from the recorded analyses of native tellurium, gold is not infrequently found to be present.

In the investigation of the tellurides, the author has been extremely fortunate in having had placed at his disposal the fine collection of tellurides of the University of Wisconsin, through

<sup>1</sup> *Am. J. Sci.*, p. 225, September, 1901.

the courtesy of Professor W. H. Hobbs, of the department of mineralogy.

In some investigations now being carried out by Hall and Lenher, on the action of metallic tellurium on gold and silver salts, it has been observed that tellurium quantitatively precipitates gold from solution in the ratio of  $4\text{Au}:3\text{Te}$ , according to the equation



When a solution of chloride of gold is added to metallic tellurium, metallic gold is deposited, tellurium tetrachloride passing into solution. The reaction is accelerated by heating the solution, and time is a considerable factor as far as quantitative results are concerned. If proper precautions are observed and the gold salt is in excess, the above ratio will be obeyed.

Likewise, when tellurium is introduced into a silver solution, similar results are obtained. The reaction, as thus far studied, appears not to be as sharp as with gold, nor as complete; nevertheless, our results have demonstrated that from a silver solution, no matter whether an aqueous solution of fused silver nitrate, ammoniacal silver nitrate, or ammoniacal silver chloride be used, metallic silver is obtained.

The action of elementary selenium on gold solutions has also been studied, and the results obtained show that selenium acts as a reducing agent to gold salts, throwing the metal out of solution.

When these facts had been ascertained, the natural tellurides were tested to determine their behavior to chloride of gold. Sixteen specimens of the minerals from different sources were tested, and in each case, when the telluride mineral was brought into contact with a chloride of gold solution, metallic gold was obtained. The minerals examined were:

One specimen calaverite, Abe Lincoln Mine, Cripple Creek, Colorado.

One specimen calaverite, Little May Mine, Cripple Creek, Colorado.

One specimen calaverite, Porcupine Mine, Cripple Creek, Colo.

Five specimens calaverite, Gold Coin Mine, Victor, Colorado.

One specimen sylvanite, Battle Creek Monument, Cripple Creek, Colorado.

Two specimens sylvanite, Magnolia, Boulder County, Colorado.

One specimen sylvanite, Offenbanya, Hungary.

One specimen coloradoite, West Australia.

Two specimens kalgoorlite, West Australia.

One specimen nagyagite, Nagyag, Austria.

All of these minerals precipitated metallic gold from the solution of chloride, and when only a small quantity of gold solution was used, the latter was bleached from yellow to completely colorless.

The question naturally arises at this point, whether a chemical compound can precipitate one of its constituents in such a manner as shown in this reaction. An attempt was then made to prepare telluride of gold artificially with a view of studying its composition and properties.

In the elaborate research of Brauner<sup>1</sup> on the atomic weight of tellurium, an attempt was made to synthesize telluride of gold. He obtained "crystalline polytellurides (alloys of gold and tellurium) of a silvery lustre," but not definite in composition.  $\text{Au}_7\text{Te}$  is the nearest approximation to a definite formula. Brauner's work has been repeated by me. Gold mixed with an excess of tellurium was placed in a porcelain boat and heated to redness in a current of carbonic acid. Under these conditions, tellurium distils on heating, and the amount given off is entirely dependent on the temperature and length of heating. After conducting this experiment for six hours, the material remaining in the boat had a golden appearance. On removing this substance, which appeared in globules, from the boat, it was found to consist of an outer shell or crust of gold, covering a white alloy-like substance. Inasmuch as this white body, on being brought in contact with chloride of gold solution, precipitates metallic gold, it is hardly likely that it is a definite chemical compound.

Another series of experiments was conducted with a view of preparing telluride of gold in the wet way. Hydrogen telluride generated by the action of dilute hydrochloric acid on aluminum telluride, was conducted into a solution of chloride of gold; a golden colored precipitate was formed. This precipitate was collected and carefully analyzed, and was found to be pure gold. The experiment was repeated, precipitating first only a part of the gold, then adding an excess of hydrogen telluride and precipitating completely. These fractions were separately analyzed, and in all cases the precipitates formed by the action of hydrogen telluride on gold solutions were found, by actual weight, to be

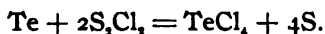
<sup>1</sup> *J. Chem. Soc.*, 88, 391.



pure gold, and in no precipitate could even a trace of tellurium be detected. According to these results, hydrogen telluride does not form telluride of gold, or at all events, telluride of gold has not appeared thus far in the wet way. All attempts which have been made thus far for the preparation of artificial telluride of gold have been unsuccessful.

At this point, it might be well to add that an attempt to precipitate gold and tellurium together has been unsuccessful. To a solution containing 0.1089 gram gold and 0.1404 gram tellurium as chlorides, sulphur dioxide was added, with the hope that possibly the compound  $\text{AuTe}_2$  might be precipitated. The result was first a precipitation of gold followed by tellurium. Had any tellurium come down at first, on coming in contact with the gold in solution, it would have precipitated the latter. The entire precipitate was collected, dried, and fused in carbon dioxide. It gave a white alloy which precipitated gold from a solution of gold chloride.

Recent work<sup>1</sup> on the action of sulphur monochloride on metallic tellurium has shown that when these two substances come in contact, tellurium tetrachloride is formed, and being insoluble in chloride of sulphur, separates in white needle-like crystals. The action is represented by the equation



The free sulphur formed as indicated in the reaction goes into solution in the excess of sulphur chloride.

The entire series of naturally occurring tellurides when subjected to the action of sulphur monochloride lost their tellurium, leaving gold as a residue, and in a number of cases the tellurium immediately separated as crystals of tetrachloride.

Another reaction of these minerals, which perhaps has not as much significance from the chemical standpoint, is that with nitric acid. When the minerals are treated with nitric acid, the tellurium and silver dissolve, leaving the gold as a residue.

#### SUMMARY.

1. Metallic tellurium quantitatively precipitates gold from solution. A similar reaction takes place with silver, though possibly not so completely. Selenium acts as a reducing agent with solutions of these metals, but is not as strong a reducing agent as tellurium.

<sup>1</sup> This Journal, 24, 188.

The tellurides of nature act towards gold solutions unlike a chemical compound of gold and tellurium, in that they throw gold out of solution.

It is not infrequent to find specimens of native gold in the same mine with the tellurides. The author has observed yellow or golden incrustations as a superficial coating on natural crystals of calaverite and sylvanite, while immediately under this coating the silver-white telluride was found; when this white material was brought into contact with gold chloride, metal was obtained.

Professor C. R. Van Hise informs the author that he has seen many beautiful specimens of gold from Cripple Creek which are pseudomorphs after the tellurides, showing both the crystalline form and striations of the original mineral.

2. Thus far the attempts to prepare telluride of gold artificially either in the wet way or the dry way have been unsuccessful.

3. It is possible to extract the tellurium from these minerals, leaving the noble metal as a residue.

#### CONCLUSIONS.

In view of the facts above ascertained, much doubt seems to be cast as to whether the tellurides are definite chemical compounds. The fact that they all precipitate metallic gold from solution, and lose their tellurium with such reagents as sulphur chloride, are points which are difficult to reconcile with a chemical compound.

The observation that hydrogen telluride in contact with gold solutions instead of forming telluride of gold, acts as a reducing agent, throwing out pure gold, may also be regarded as significant, and as well the fact that the body of inconstant composition containing tellurium and gold, obtained at high temperatures, reduces gold chloride, appears to place the telluride minerals in a very doubtful light as chemical compounds.

UNIVERSITY OF WISCONSIN,  
MADISON, WIS.

#### SOME COMPOUNDS OF PYRIDINE.

BY J. ARTHUR HAYES.

Received January 6, 1902.

WHEN some compounds of the metals with the halogens, in solution of that halogen acid, are brought in contact with the halogen acid compound of pyridine, addition-products

are formed of a crystalline structure, the composition varying with the method of preparation.

In view of this fact the author has been able to prepare several compounds of pyridine, the following of which have not been described :

THE COMPOUND  $C_5H_5N.SbBr_3.3HBr$ .

Pyridine hydrobromide is prepared by adding hydrobromic acid to pyridine, an excess of acid being used to prevent crystallization. As considerable heat is evolved, the vessel containing the hydrobromide is cooled under the tap, and then a solution of antimony bromide in hydrobromic acid is added with caution.

Upon the addition of the acid solution of antimony bromide to the pyridine hydrobromide, there is more evolution of heat and the formation of a yellow crystalline precipitate. This is allowed to stand for a time to insure complete precipitation and then filtered off by means of a suction-pump. For purification the salt is stirred in a vessel with ethyl alcohol (95 per cent.), and again filtered and washed with alcohol until the filtrate contains no traces of free pyridine, antimony or hydrobromic acid.

The antimony was determined as the sulphide and the bromide by titration with decinormal silver nitrate with potassium chromate as an indicator. Pyridine and the hydrogen of the compound were obtained by difference.

An average of several analyses gave :

	Calculated for $C_5H_5N.SbBr_3.3HBr$ .	Found.
Antimony.....	17.6	18.5
Bromine .....	70.3	70.4
Pyridine and hydrogen.....	12.1	11.1

*Properties.*— $C_5H_5N.SbBr_3.3HBr$  is in the form of small yellow crystals. It is soluble in dilute hydrochloric acid, insoluble in ether and benzene; very slightly soluble in ethyl alcohol and chloroform.

When treated with nitric acid the oxide of antimony is formed; when treated with water a basic hydroxide of antimony is formed, and heating the salt dry decomposes it to the oxide of antimony.

THE COMPOUND  $C_5H_5N.SnCl_4.3HCl$ .

*Preparation.*—The process is the same as for the preparation of the antimony salt with the exception of hydrochloric acid, in-

stead of hydrobromic being used as a solvent for the metallic salt and to form the acid halogen salt of pyridine.

The analysis gave :

	Calculated for $C_5H_5N.SnCl_2.3HCl$	Found.
Tin .....	28.07	28.5
Chlorine .....	50.20	50.75
Pyridine and hydrogen .....	21.73	20.75

*Properties.* —  $C_5H_5N.SnCl_2.3HCl$  crystallizes in small white needle-shaped crystals. It is decomposed by water into a basic hydroxide or oxide of tin, and by nitric acid into the oxide of tin. When heated, the oxide of tin is the decomposition product. It is soluble in dilute hydrochloric acid, insoluble in ether, benzene, and chloroform, and very slightly soluble in 95 per cent. alcohol.

#### THE COMPOUND $C_5H_5N.MnCl_2.HCl$ .

*Preparation.* — The process is the same as for the preparation of the tin salt. A great deal of care has to be taken in the purification by 95 per cent. alcohol as the compound is quite soluble. The manganese was determined by precipitation with sodium carbonate and was weighed as  $Mn_2O_3$ .

The analysis gave :

	Calculated for $C_5H_5N.MnCl_2.HCl$	Found.
Manganese .....	22.70	21.57
Chlorine .....	44.00	44.70
Pyridine and hydrogen .....	33.30	34.33

*Properties.* —  $C_5H_5N.MnCl_2.HCl$  crystallizes in salmon-colored plates. It is soluble in 95 per cent. alcohol and hydrochloric acid, slightly soluble in ether and insoluble in chloroform. When heated, decomposition takes place with the formation of the oxide of manganese.

UNIVERSITY OF MAINE CHEMICAL LABORATORY,  
June 1901

### COMMON ERRORS IN THE DETERMINATION OF SILICA.

By W. F. HILLEBRAND.

RECEIVED JANUARY 6, 1902.

TO some it may seem as if a threadbare subject had been reopened in the above title, and that concerning a determination of such common occurrence in both technical and scientific

Read at the Philadelphia meeting of the American Chemical Society.

operations little remained to be said or done. But that this is not so the following presentation will, I think, make sufficiently clear. Although not much of what I shall offer is really new, even that which is not will well bear repetition, having escaped the attention which it deserves. It seems to be advisable and necessary that public attention should be from time to time called to important facts which have not impressed themselves sufficiently to become a matter of common knowledge and application.

Regarding certain features of the silica determination I have long entertained doubts, but it is only very recently that convenient opportunity has presented itself for an investigation of these points as well as others, the direct incentive being afforded by an experience of the past summer as an outgrowth of the labors of a Committee of the New York Section of the Society of Chemical Industry having for its object the promotion of uniformity in technical analysis.

Uniform samples of raw cement-mixture and of finished cement were sent to a large number of analysts for determination of the commoner constituents by the usual technical methods. The same samples were analyzed in greater detail by myself and with the same regard to exactness that is usual in analyzing rocks and minerals in the laboratory of the United States Geological Survey. Fourteen of the chemists besides myself returned reports which showed in most cases a marked lack of agreement. The results for silica<sup>1</sup> only are here presented in tabular form with one exception, which is omitted for the reason that it does not profess to represent silica only, but rather the residue from evaporation of the limestone with acid, hence containing much undecomposed mineral matter.

TABLE I. SILICA FOUND BY DIFFERENT ANALYSTS IN THE SAME SAMPLES OF RAW MIXTURE AND FINISHED CEMENT.

	Limestone mixture.	Finished cement.
Standard.....	15.18	21.31
1 .....	15.75	20.90
1a .....	15.37	—
2 .....	14.68	20.92

<sup>1</sup> The full data together with copies of the outlines of methods employed were submitted to me for review and suggestion without knowledge on my part of the names of the analysts. My report was transmitted through the Director of the Geological survey to the committee of the New York Section of the Society of Chemical Industry, and its report was rendered at the Section meeting on December 20, 1901, and published in the *J. Soc. Chem. Ind.*, Jan. 15, 1902.

	Limestone mixture.	Finished cement.
3 .....	13.92	20.06
4 .....	—	20.00
5 .....	14.18	20.26
6 .....	14.70	20.96
7 .....	12.78	20.84
8 .....	13.97	19.82
9 .....	14.44	20.76
10 .....	13.60	19.18
11 .....	14.64	21.46
12 .....	14.18	20.76
13 .....	14.92	21.56
14 .....	13.56	19.53
Highest.....	15.75	21.56
Lowest.....	12.78	19.18
Difference.....	2.87	2.38

Without detailing the various means employed for rendering silica insoluble it may be said that all the workers strove to bring this about by the usual more or less approved methods of drying at temperatures ranging from that of the steam-bath for a long time to 120° and even higher for a shorter time. Despite their efforts there is not only a wide discordance in results, but, with two exceptions in each series, they are all too low. The actual failure to recover all silica is, however, in the majority of cases greater than the figures indicate, by reason of neglect of blast-ignition, or of correction by hydrofluoric acid, or both.

It is evident then that none of the methods in common use for rendering silica insoluble can be at all depended on to effect this result. None of the analysts except No. 1 and myself seems to have employed two evaporations with an intervening filtration. All others made but a single filtration, and in this simple difference lies the main solution of the trouble, a fact pointed out by Alex. Cameron with quantitative demonstrations nearly eight years ago,<sup>1</sup> but which has apparently almost escaped the notice of chemists. Indeed I must admit a certain degree of remissness myself, for I have but an indistinct recollection that it was the reading of Cameron's paper when it first appeared which led me to adopt the practice of double evaporations with intervening filtrations which I have followed for a good many years. What influenced this change had escaped my mind until mention of

<sup>1</sup> *Chem. News*, 69, 171 (1894).

Cameron's paper in a recent number of this Journal, followed by its reperusal, recalled the matter to recollection.

Other earlier writers, as Lindo, Craig, and Gilbert, have recognized the impossibility of recovering all silica by one evaporation, without, however, recommending a repetition after filtration. Instead, dehydration by hot sulphuric acid is often used in iron and steel works, but its use precludes satisfactory determination of other constituents in the same sample.

Cameron used in most of his experiments 2 grams of silica, about 98½ per cent. pure, fused this with 9 grams of fusion mixture, dissolved the fused mass in hydrochloric acid, and evaporated in porcelain on the water-bath. The drying was continued on the bath in several experiments for some time after all acid fumes had ceased; in others the dehydration was effected by the blue flame of an Argand burner. He found that with the lower temperature four, and even five, evaporations and filtrations were needed to reduce the silica recovered to a negligible quantity, but that with the higher heat three, or even sometimes two, sufficed. Furthermore, he showed by one experiment that a very common practice of evaporating several times to dryness with fresh portions of acid without intervening filtrations did not reduce the silica in the filtrate, and that the presence of aluminum, iron and calcium was without influence on the results.

My own experiments to test all these points were entirely confirmatory of Cameron's, though less unfavorable as to the number of evaporations needed. This I attribute to the facts that I employed from one-half to one-fourth as much silica as he did, thus conforming more nearly to the ordinary conditions of a silicate analysis, and platinum instead of porcelain evaporating dishes. On the water- or steam-bath drying is not so speedily reached in porcelain as in platinum, and very possibly his later siliceous residues came in large part from the vessel itself.

The material employed in my tests was very nearly pure quartz crystal containing 99.88 per cent. silica. Amounts of this lying usually within the limits 0.5 and 1 gram were fused with 5 grams sodium carbonate, the fused masses dissolved in hot water, then acidified by hydrochloric acid, and the solutions evaporated in platinum vessels for different lengths of time on a steam-bath. Then the residues were digested for a short time with hydrochloric acid and hot water. Prolonged digestion was unnecessary, as

only sodium chloride with mere traces of other salts had to be extracted.

TABLE II. SILICA FOUND IN FILTRATES.

	Weight of quartz	SiO <sub>2</sub> in first filtrate.	Per cent.	SiO <sub>2</sub> in second filtrate.	
1..	0.8943	0.0078	= 0.87	0.0012	Duration of first drying not known. Duration of first drying brief, not exceeding one to two hours, and in one case the residue still some- what moist in parts.
2..	0.8208	0.0321	= 3.91	0.0006	
3..	0.6401	0.0218	= 3.41	0.0005	
4..	0.5738	0.0197	= 3.43	0.0009	
5..	0.7028			0.6000	Duration of first and second dry- ings twenty-one hours each. In 9 the mass was ground to powder as soon as free from visible mois- ture, without marked improve- ment in the result.
6..	0.5931	0.0167	= 2.82	0.0001	
7..	0.7309	0.0211	= 2.89	0.0001	
8..	0.8495	0.0204	= 2.40	0	
9..	0.7841	0.0142	= 1.81	?	Several evaporations with fresh acid before first filtration. Total dura- tion of dryings and evaporations twenty hours.
10..	0.7092	0.0089	= 1.25	0.0004	
11..	0.7324	0.0047	= 0.64	0.0005	Repeated (4) evaporations with wa- ter only before first filtration, twenty hours' drying before third filtration.
12..	2.0000	0.0193	= 0.96	0.0008	

Experiment 10 was made in order to test the somewhat prevalent practice of evaporating several times with fresh acid before filtering. The result is an improvement over all but the first of the earlier ones, but still leaves much to be desired.

Experiments 11 and 12, in which repeated evaporations with water only were made, show a still better but by no means satisfactory result. The improvement in these last cases is not surprising, but it is to be expected that in ordinary analysis the foreign matter remaining with the silica would be increased by this treatment with water only instead of acid.

In order to learn, if possible, something about the effect of the large amount of sodium chloride in preventing the dehydration of silica, a soluble gelatinizing zeolite (thomsonite with 41.17 per cent. silica) was experimented with. The foreign chlorides in solution were here, of course, very much reduced in amount. The results are shown opposite 1, 2, 3 of table III.



TABLE III. SHOWING DIFFERENT SOLUBILITIES OF THE SILICA SEPARATED IN GELATINOUS AND GRANULAR FORM FROM ZEOLITES.

	SiO <sub>2</sub> in weight of zeo- lite taken.	SiO <sub>2</sub> in first filtrate.	Per cent.	
1.....	0.4185	0.0065	1.55	Duration of drying 2 hours.
2.....	0.4142	0.0048	1.16	Duration of drying 21 hours.
3.....	0.8265	0.0072	0.87	Duration of drying 21 hours.
4.....	0.5736	0.0020	0.35	Duration of drying brief.
5.....	0.5760	0.0023	0.40	Duration of drying prolonged.

Since the separation of silica from soluble silicates occurs in two forms, gelatinous and granular, according to the species acted on, it seemed worth while to try a non-gelatinizing zeolite (heulandite) containing 57.18 per cent. silica. The results appear opposite Nos. 4 and 5 of Table III. Manifestly the instantaneous separation of silica in granular form, without first entering into solution, is far more perfect than when it gelatinizes.

We have thus seen how the serious errors in silica determinations shown by Table I can be avoided by two evaporations with intervening filtrations. In extreme cases a third evaporation may at times be advisable. Furthermore, that prolonged drying is a useless waste of time, except perhaps after the second evaporation, when, if results like 6, 7, and 8 of Table II can be depended on, it may be of value in very exact work.

#### CAUSES OF THE SOLUBILITY OF SILICA UNDER THE CONDITIONS GIVEN.

In explaining the partial solubility of silica after drying at temperatures much above that of the water-bath it has been customary to assume the formation of soluble silicates by action between some of the silica and salts present. This is an undoubted cause and one which should become more active with increasing temperature, though Gilbert's work does not seem to indicate this except when magnesium is present in quantity. But if true at 120° it must probably still be true to some extent at 100°.

Another explanation for the incomplete dehydration at 100° is assumed to be the protecting influence of other salts, and to remedy this, repeated additions of acid, or perhaps better still of water, are sometimes resorted to (See Exp. 10-12 of Table II).

Again it may be that the silica separated is itself soluble enough in acid to cause an appreciable error. The experiments reported below show clearly what the action of hydrochloric acid is on silica which had been obtained by fusing quartz with sodium carbonate and drying the evaporated hydrochloric solution for twen-

ty-one hours on the steam-bath. This silica (about 0.65 gram) was first extracted with a little acid, then thoroughly washed with hot water, rinsed back into the dish, and digested with hydrochloric acid of about 1.10 sp. gr. under varying conditions.

*a.* Digested twenty-five minutes on steam-bath with about 25 cc. acid. Silica in filtrate 0.0029 gram.

*b.* Same silica further treated as in *a* for one and one-half hours. Silica in filtrate 0.0026 gram.

*c.* Same silica gently boiled in platinum for thirty minutes with above acid. Silica in filtrate 0.0022 gram.

There was thus extracted with ease nearly 1.2 per cent. of the total silica without counting the probably larger amount held by the original filtrate, and it is to be presumed that the effect of the boiling would have been greater had it preceded instead of followed the quiet digestion.

It is thus plain how a portion of the silica always found in the filtrates gets there and that it is hopeless to try to prevent this by a single prolonged drying. Once the bulk of the silica is removed by filtration, however, then, after a second evaporation, because of its tendency to collect in clots of sensible size and consequent small surface exposure, the amount of silica going into solution is very small and by no means in proportion to that of the acid used.

#### DETERMINATION OF SILICA THAT HAS ESCAPED SEPARATION BY THE USUAL PROCESSES OF DEHYDRATION.

I pass now to another phase of the determination of silica, which so far as I am aware, has never been investigated.

While it has long been known that some silica passed into the filtrate in silicate work, it was supposed to be recovered in the ordinary course of analysis with the ammonia or basic acetate precipitate, whence after ignition and weighing it could be obtained in insoluble form by fusing the mixture with potassium pyrosulphate. I purpose showing that these suppositions are both in part erroneous, that the residual silica is, as Lindo says,<sup>1</sup> not

<sup>1</sup> Lindo (*Chem. News*, 60, 14 (1889)) gives no quantitative data and in all his experiments (with glass) the ammonia precipitates were, of course, very small. It is fair to conclude from his addition of ferric chloride to the filtrates from them in order to recover by its precipitation by ammonia the "last trace" (*loc. cit.*, p. 40) of silica, that he would not have suspected the presence of any silica in these filtrates when analyzing mixtures containing considerable aluminum or iron oxide. Lindo's observations are of value, but his analytical results are not, for the reason that he operated largely in glass vessels and his alkaline solutions remained long in contact with glass, hence must have taken silica from them, notwithstanding which his analyses show without exception a large loss.

wholly precipitated by ammonia, and that the ordinary treatment of the pyrosulphate fusion mass recovers but a minor part of that which was thrown down with the oxides of iron and aluminum.

The experiments of the following table were made with a hydrochloric solution containing 0.0101 gram of silica in 10 cc. and with a solution of aluminum chloride free from silica. The amounts used were chosen to represent approximately the conditions most frequently prevailing in silicate analysis after but a single evaporation to separate silica. Precipitation was effected by ammonia at boiling temperature in a solution of about 300–400 cc. volume containing 25 cc. hydrochloric acid of 1.10 sp. gr. As soon as settled the alumina was filtered, washed, ignited, and fused with potassium pyrosulphate free from silica. The fused mass was generally dissolved in hot water acidulated with sulphuric acid, and once in warm water only, and the residual silica was collected, weighed, and corrected by hydrofluoric acid. In two cases (8 and 9) the filtrates were evaporated with excess of sulphuric acid, heated till fumes came 'off in quantity, and the separated silica collected after cooling and dilution of the solution. The filtrates from the alumina were evaporated, ignited to remove ammonium chloride, and the silica recovered by evaporation with a few drops of hydrochloric acid and further treatment as usual.

TABLE IV. SILICA IN ALUMINA AND IN FILTRATE FROM ALUMINA AFTER ONE PRECIPITATION BY AMMONIA.

	Al <sub>2</sub> O <sub>3</sub> used.	SiO <sub>2</sub> used.	SiO <sub>2</sub> in filtrate.	SiO <sub>2</sub> recovered from Al <sub>2</sub> O <sub>3</sub> .	SiO <sub>2</sub> recovered from K <sub>2</sub> S <sub>2</sub> O <sub>7</sub> solution.
1.....	0.19	none	none	none	....
2.....	0.19	0.0101	....	0.003	....
3.....	0.19	0.0101	....	0.0037	....
4.....	0.19	0.0101	0.0020	....	....
5.....	0.19	0.0101	0.0021	....	....
6.....	0.19	0.0101	0.0007	0.0034	....
7.....	0.19	0.0101	0.0019	0.0021	....
8.....	0.20 <sup>1</sup>	0.0101	0.0007	0.0033	0.0060
9.....	0.19	0.0101	0.0021	0.0023	0.0058

Treatment of about 0.01 gram of ignited precipitated silica with fused pyrosulphate resulted in the solution of 2 mg. of it and of 2.2 mg. in another test. Not being evenly distributed through a mass of other oxides undergoing solution the solvent

<sup>1</sup> Fe<sub>2</sub>O<sub>3</sub>.

effect of the pyrosulphate in these cases may reasonably be supposed to be less than in the tests of the table.

We here see how in practically all ordinary silicate analyses a portion of the silica, sometimes very small, escapes being weighed at all, since it mostly passes on into the filtrate from the magnesia. When a double precipitation by ammonia or sodium acetate is made, instead of one as in the above tests, the loss will be greater than the table shows.

We further see how, when correction is made for the silica with the alumina, it is only in small part recovered and the alumina is consequently made to appear too high when determined indirectly. Here we have an added argument in favor of endeavoring to collect all silica at the outset, for it is shown that the expectation of recovering the whole of a missing portion later is based on erroneous assumptions. Therefore Gilbert's conclusion, because he found very little silica with the alumina after fusion with pyrosulphate, that there is "no tendency for silica to recombine with the lime and alumina" (in non-magnesia silicates) "even at a temperature of 280° C."<sup>1</sup> is perhaps not well founded. Since his further conclusion that silica is almost completely dehydrated at 120°<sup>2</sup> is based on this same reason, his analytical results lose much of their value.

As showing the errors in the silica results that may be incurred in the analysis of certain siliceous ores where potassium pyrosulphate is employed as the means for breaking them up, I will here give the figures for two titaniferous magnetites. The lower values give the silica obtained in the usual way from the mixture of silica and silicates left after fusion with pyrosulphate, and the higher those afforded by direct fusion of the ores with sodium carbonate.

	I.	II.
Silica .....	{ 11.73	20.82
	{ 12.42	21.42

Complete analysis of the ores showed such a deficiency when pyrosulphate was used that the cause was sought and found to be as stated above. It was this observation which led to a portion of the work summarized in Table IV.

<sup>1</sup> *Technology Quarterly*, 3, 63 (1890).

<sup>2</sup> *Loc. cit.*, p. 64.

## THE PROPER TEMPERATURE FOR IGNITION OF SILICA.

Most authorities, Fresenius included, have directed that blast temperatures be used in order to obtain the correct weight of ignited silica. It is only recently that doubt has arisen as to this because of the experiments of Lunge and Millberg,<sup>1</sup> who, employing silica derived from silicon tetrafluoride, observed no further loss in weight over the blast after sufficient exposure to the full flame of a good Bunsen lamp. This was in direct conflict with all my experience in silicate work, and as a result of friendly correspondence Professor Lunge caused the matter to be reinvestigated in his laboratory a year ago and sent me the following table of results, which I take the liberty of making public.

TABLE V.—LOSS IN WEIGHT OF PURE SILICA FROM  $\text{SiF}_4$ , AT DIFFERENT TEMPERATURES AS DETERMINED BY DR. LOHÖFER, IN PROFESSOR LUNGE'S LABORATORY.

Temperature.	Time. Minutes.	a.	b.	c.
105°	..	0.1840	0.1778	0.2020
Dark redness	30	0.1643	0.1584	0.1803
Dark redness	30	0.1640	0.1584	0.1800
Full flame of burner	30	0.1622	0.1566	0.1779
Full flame of burner	30	0.1620	0.1564	0.1778
Blast	30	0.1619	0.1564	0.1776

It is but natural that Professor Lunge should write: "From these results I must conclude that Millberg and myself were right."

The following two tests by myself on silica similarly obtained confirm the above, and show, after blasting, further slight losses comparable with those appearing in Professor Lunge's table and of the same order as those produced by more than half an hour's blasting with silica precipitated by acid (see Table VIII).

TABLE VI.—SHOWING LOSS IN WEIGHT OF PURE SILICA FROM  $\text{SiF}_4$ , ACCORDING TO TESTS MADE BY MYSELF.

	a.
	0.5053
Full burner flame 30 minutes .....	0.5017
Blast flame 30 minutes.....	0.5014
	b.
	0.5030
Full burner flame 45 minutes .....	0.4997
Full flame 45 minutes .....	0.4995
Blast flame 40 minutes.....	0.4991 <sup>2</sup>

<sup>1</sup> *Ztschr. angew. Chem.*, p. 425 (1897).

<sup>2</sup> This loss is partly chargeable to the crucible itself.

These slight losses are not due to mechanical carrying off of silica, for the latter had utterly lost its extraordinarily down-like character during the early heating and become converted by the blasting into a coherent cake of enormously reduced bulk.

Let me now, however, present another series of results furnished by silica otherwise precipitated. The silica used was obtained by three evaporations from the quartz that served for the earlier experiments of this paper, and the initial weights are those found after an exposure of about one hour to the full Bunsen flame. The weights given represent the silica as corrected by hydrofluoric and sulphuric acids for the few tenths of a milligram of non-volatile salts always present. The crucibles were found not to lose weight themselves over the blast. The quartz powder employed was 99.88 per cent. pure, as found by careful evaporation with hydrofluoric and sulphuric acids.

TABLE VII.—SHOWING DIFFERENCES IN WEIGHTS OF SILICA PRECIPITATED FROM SODIUM SILICATE WHEN IGNITED OVER BUNSEN BURNER AND BLAST-LAMP.

No.	Weight of quartz.	Silica found.		Loss in weight.	Percentages found.	
		Burner 1 hr.	Blast ½ hr.		Burner.	Blast.
1	0.5738	0.5761	0.5735	0.0026	100.40	99.95
2	0.5931	0.5945	0.5930	0.0015	100.24	99.98
3	0.6401	0.6450	0.6394	0.0056	100.76	99.90
4	0.6638	0.6668	0.6628	0.0040	100.45	99.85
5	0.7028	0.7058 <sup>1</sup>	.....	.....	100.25	....
6	0.7309	0.7342	0.7306	0.0036	100.45	99.96
7	0.8208	0.8271	0.8206	0.0065	100.77	99.98
8	0.8495	0.8521	0.8484	0.0037	100.31	99.88
9	0.8943	0.8996	0.8936	0.0060	100.59	99.92
10	.....	0.9989	0.9898	0.0091	.....	....

Results similar to the above are repeated in every silicate analysis that is made in our laboratory, and others have told me their experience is the same. It is as clear as daylight that the blast is a necessity if the work is to be at all accurate. In every one of the above instances the percentage found without blast is far in excess of 99.88, the true value for silica in the quartz, and is as invariably brought very near this value and with far smaller variations from a mean when the blast is applied (see further, p. 373). The above values for "burner" percentages very well represent the usual lack of exact agreement in series of duplicate silica determinations, when the blast has not been used (see Gil-

<sup>1</sup> Two hours.

bert's paper), while those of the next column show of what accuracy the determination is susceptible when all the conditions of success are understood and applied.

From the foregoing it appears that the silica separated by water from silicon tetrafluoride and that by hydrochloric acid from sodium silicate are in different conditions and behave differently when strongly heated; that Professor Lunge's conclusion that silica need not be blasted, while correct for one form of silica, cannot be applied, as he supposed, in analytical work.

I have always, until lately, regarded one-half hour's blasting as sufficient in all cases for as much as a gram of silica, but that this length of time is often insufficient to secure constant weight is indicated by some of the results in Tables V and VI and still more by those in the following :

TABLE VIII.—SHOWING NEED OF VERY LONG BLASTING AT TIMES.

Heat.	Time in minutes.	Weights of silica.					
		1.	2.	3.	4.	5.	6.
Burner	60	0.6691	0.7041	0.9989	.....	0.4175	0.4220
Blast	30	0.6657	0.6982	0.9905	0.7208	0.4154	0.4192
Blast	30	0.6656	0.6979	0.9902	0.7201	.....	0.4187
Blast	30	0.6651	.....	0.9899	0.7193	0.4152	0.4185
Blast	30	.....	.....	0.9897	0.7194	.....	.....
Blast	30	.....	.....	.....	0.7194	.....	.....

The progressive losses shown here are not chargeable to the crucibles, nor were they due to mechanical loss of silica or to volatilization of included salts, and they explain very well the fact that nearly all the figures of the first column in Table V slightly exceed the true value for silica in the quantity used, for they were obtained by blasting for only one-half hour. They may also serve to explain in small part the excessive summations often encountered in rock analyses. These later losses can exert little effect when the silica percentages are small, but when large, as in rock analysis, they may at times be of moment and necessitate blasting for more than half an hour.

In the foregoing I have entered into such detail as the exact scientific worker needs for his enlightenment and have carried my separations and ignitions farther than the technical chemist ordinarily cares to or can proceed. But in its main features, what I have said concerns him not less than the research chemist and I trust that in some respects it may help to ease his path.

## SUMMARY.

Statements of earlier writers are fully confirmed, that silica cannot be rendered wholly insoluble by a single or any number of evaporations with hydrochloric acid when followed by a single filtration, no matter what temperature may be employed, but that two or more evaporations alternating with filtrations are necessary to secure satisfactory results.

It is shown that the generally accepted view that any silica passing into the filtrate is wholly thrown down by ammonia or sodium acetate in presence of much aluminum or iron is incorrect. Also that silica is appreciably soluble in melted potassium pyrosulphate and that consequently when siliceous oxides of iron and aluminum obtained in analysis are then fused their silica contents are only in small part left undissolved when the fused mass is taken up with water or acid. Both these sources of error are avoided by separating all silica at the start as above.

The need of blast ignition in order to get the correct weight of silica obtained in analysis is proved. The opposite conclusion of Lunge and Millberg, being based on what seems to be a different behavior of the silica derived from silicon tetrafluoride, is therefore not justified.

LABORATORY U. S. GEOLOGICAL SURVEY,  
December, 1901.

---

[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF HARVARD COLLEGE.]

A REDETERMINATION OF THE ATOMIC WEIGHT OF CALCIUM—PRELIMINARY PAPER.

BY THEODORE WILLIAM RICHARDS.

Received February 16, 1902.

**D**URING the years 1897 to 1899 an investigation upon the atomic weight of calcium was conducted in the Chemical Laboratory of Harvard College. This investigation was more carefully conducted, and in some respects more elaborate than any previous research of a similar kind conducted in this laboratory. The details are so many that time has not yet been found for a verbal presentation of them, but a brief report of the results was made to the American Association for the Advancement of Science in August, 1899, of which a notice is published in the journal.<sup>1</sup>

<sup>1</sup> This Journal, 22, 72 (1900).



Very recently there has appeared the account of a careful investigation of calcium carbonate made by Hinrichsen under the direction of Landolt.<sup>1</sup> Since this investigation confirms the outcome of the Harvard research, a brief preliminary account of this may be interesting. It is hoped that later the details may be presented in full.

In spite of the common occurrence of the element calcium, its atomic weight had been investigated only in a partial and incomplete manner. The chief work upon the subject has consisted of the quantitative ignition of calcium carbonate, and it seemed important to obtain also data of a radically different kind. Because of the peculiar properties of the halides of silver, most of the accurately determined atomic weights of other metals have been found by the analysis of their respective halides, and it would evidently be worth while to include calcium in this series. The old work of Dumas is, of course, of no importance, because of his faulty comprehension of the method of Gay-Lussac.

Accordingly the present series of determinations consisted of the analysis of calcium chloride, the silver chloride obtained from a known weight of the anhydrous salt being collected and weighed with care.

The first problem to be solved was the preparation of pure calcium chloride. Preliminary experiments showed that calcium nitrate is the best salt to use for recrystallization, because of its rapid variation of solubility with the temperature, and because of the fact that the corresponding salts of magnesium, strontium, and barium do not crystallize out with it. Two portions of marble were used as the starting-point, one came from Rutland, Vermont, U. S. A., while the other was a specimen of the purest Italian marble taken from a ship which had just arrived at the port of Boston. The Rutland marble was converted into the nitrate, and from this specimen, after preliminary purification with lime, etc., two samples were prepared, one having been carefully recrystallized ten times, and the other twenty times.<sup>2</sup>

The single specimen of pure nitrate from the Italian marble was recrystallized fifteen times, thus being comparable with the

<sup>1</sup> *Ztschr. phys. Chem.*, 39, 311 (1901).

<sup>2</sup> The process of recrystallization was kindly conducted by M. J. B. Churchill, who also made the preliminary experiments, showing the degree of purity to be obtained in this way.

average of the American samples, in case any difference between them might exist.

The metal in each of these specimens was precipitated as carbonate by the purest ammonium carbonate, and then converted into chloride. After four recrystallizations the chloride was dried, ignited in a porcelain tube in a stream of hydrochloric acid gas to render a possible trace of silica insoluble, dissolved, filtered, and crystallized twice more. Of course platinum vessels were used throughout, and every precaution was taken to insure a close approach to that perfect purity which is unattainable.

The three samples of material which had been thus made ready were dried for analysis by prolonged ignition and final fusion at a bright red heat in a porcelain tube. The hydrochloric acid gas, which had been added to the nitrogen in the tube to prevent loss of chlorine, was then wholly displaced by the inert gas, and when the apparatus was nearly cold this was driven out by dry air. After having been transferred to the stoppered weighing-bottle by means of the convenient automatic bottling apparatus so much used at Harvard, it was weighed and analyzed. The correction for the solubility of the silver chloride was determined much as in the case of barium chloride, several years ago.

The results show that the three samples of calcium chloride (which were wholly neutral to methyl orange) were essentially identical. Hence neither a change in the source of the material nor repeated fractionation causes any variation in the atomic weight. The following table contains the weights of material, reduced to the vacuum standard, and the calculated results.

#### THE ATOMIC WEIGHT OF CALCIUM.

O = 16.000; Cl = 35.455.

No.	Weight of $\text{CaCl}_2$ in vacuum.	Weight of $\text{AgCl}$ in vacuum.	Atomic weight of calcium.
1	1.56454	4.0409	40.121
2	3.57630	9.2361	40.130
3	3.59281	9.2788	40.129
4	5.00880	12.9364	40.124
5	9.00246	23.2506	40.125
Average,			40.126
American (10 crystallizations), Nos. 2, 5.....			40.127
American (20 crystallizations), No. 4 .....			40.124
Italian (15 crystallizations), Nos. 1, 3.....			40.125

The results thus agree closely with the value 40.142 since obtained by Hinrichsen, who was not cognizant of my work. A further investigation is now being undertaken at Harvard to show whether other methods, executed with great care, support or discountenance this high value.

### COMMERCIAL AQUA AMMONIA, ITS EFFECT UPON IRON, ITS IMPURITIES, AND METHODS FOR DETERMINING THEM.

By J. D. PENNOCK AND D. A. MORTON.

Received January 10, 1908.

THE very extensive development of refrigerating plants, large and small, throughout the country during the last decade has greatly increased the manufacture of aqua ammonia.

Formerly aqua ammonia of 26° Bé., or 29.0 per cent.  $\text{NH}_3$ , was shipped in carboys. The shipments of aqua soon became so large that it was no longer practicable to transport in such cumbersome and fragile receptacles, and recourse to metal carriers was had. But ammonia was known to attack most metals seriously. W. R. Hodgkinson and N. E. Bellairs<sup>1</sup> found that all metals which form soluble double salts with ammonium salts are most acted upon by ammonia solution. Zinc, nickel, and cobalt are, after copper, most rapidly attacked. Lead dissolves more slowly, and iron, aluminum, and magnesium do not appear to dissolve at all.

Lunge says<sup>2</sup> that aqua ammonia in contact with iron, "gives rise to red precipitates of iron oxides."

Lunge's opinion was evidently held by European ammonia manufacturers, for in one of the larger works that the writer visited in Belgium in 1897, the absorber for the ammonia gas was a lead-lined vessel, and the aqua produced was shipped in carboys.

The opinion was held by certain manufacturers that aqua made from the distillation of sulphate of ammonia with lime would not attack iron, but that aqua made from crude ammonia liquor would.

To ascertain the effect of ammonia on iron and determine if an iron absorber could be used in place of a lead one, and if aqua could be shipped in iron drums and iron cars, various experiments

<sup>1</sup> *Proc. Chem. Soc.*, 9, 146 (1895).

<sup>2</sup> "Coal-Tar and Ammonia," p. 685.

were undertaken. In these experiments, (1) absolutely C. P. aqua, made from C. P. sulphate, distilled with C. P. lime into distilled water, (2) the ordinary commercial aqua, made from sulphate, and (3) several samples, containing different percentages of impurities, all made from the direct distillation of crude liquor without first forming the sulphate, were used.

To ascertain the effect of these different ammonia solutions upon iron, small bottles, 7 inches high and 1.5 inches in diameter, were partly filled with the ammonia solution, and a bright nail, carefully cleaned by filing, was introduced into the solution, and left in contact with it twenty-four hours before examination.

The composition of the ammonia solutions used was:

1. Practically chemically pure aqua, containing 28 per cent.  $\text{NH}_3$ .
2. Aqua from sulphate, containing organic matter equivalent to 10 cc. centinormal potassium bichromate per 100 cc. aqua, 0.046 gram per liter carbon dioxide, no chlorine, no sulphate, 2 grams per liter pyridine, and 28.5 per cent.  $\text{NH}_3$ .
3. Thirteen samples of aqua from crude liquor containing organic matter equivalent to from 5 to 80 cc. potassium dichromate, carbon dioxide from 0.1 to 2 grams per liter, chlorine 0.0 to 0.1 gram per liter, and pyridine, 0.1 to 5 grams per liter, and 28.5 per cent.  $\text{NH}_3$ .

Upon examining the samples after exposing twenty-four hours, it was found that the C. P. aqua, that made from sulphate, and eight of those made from crude liquor, remained perfectly clear, and the iron was in no way acted upon; but that five were badly attacked, the nail being decidedly rusty, and the solution cloudy with reddish yellow oxide, very finely divided, which remained in suspension and would not settle. It was thought the nails had not been perfectly cleaned, because the composition of the ammonia solutions was so slightly different; five other nails were put into fresh solutions of the same kind, and after twenty-four hours all remained perfectly bright, and the solutions perfectly clear, showing that metallic iron, if perfectly free from specks of rust, is unattacked by strong solutions of ammonia, even if these solutions contain 2 grams per liter carbon dioxide, 5 grams per liter pyridine, and a high percentage of organic matter.

But, of course, it is impossible to so treat the inside of an iron absorber, a drum or tank, that its surface shall be entirely free

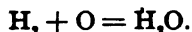
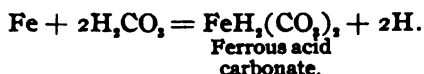
from rust, and consequently when one begins to make aqua ammonia in an iron absorber, or ship it in drums or tank cars, reddish precipitates of iron oxide, which settle with great difficulty, are formed.

Further experiments with iron nails in different stages of oxidation were made with the same solutions, and it was found that a nail freshly rusted forms immediate and continued discoloration of the aqua, while a nail with a thick coating of old rust completely covering the iron does not influence the ammonia solution in the slightest degree.

To be able therefore to absorb strong ammonia solution in an iron vessel, or to ship it in drums or tank cars, it is necessary in some way to coat the surface of the iron with an oxide. This is not an easy matter. Boiling the drum in a weak solution of permanganate of potash will do it, but this is expensive. It has been found, from experiment, however, that by continuous use of the iron absorber, or by repeatedly shipping in drums or cars, this desirable coating is formed, and the aqua is finally not discolored. In the language of the factory, the tank becomes "seasoned," and when this has taken place there is no further trouble from discoloration by iron oxides.

For the rusting of iron it is necessary that water, carbon dioxide, and oxygen, must come in contact with the metal.

The reactions illustrating its formation are :



Only traces of carbon dioxide and water are necessary to cause continuous rusting.

In the above reaction it is free carbonic acid that reacts with the iron. In ammonia solutions there can be no free carbonic acid, as all carbon dioxide, even in the air above the liquid, is present as ammonium carbonate. It seems quite possible that the weak affinity of iron for carbonic acid would not be sufficient to remove the latter from ammonium carbonate; in other words, it is only free carbonic acid that is available for rusting iron.

All of our experiments with aqua have verified the following conclusions :

A. Concentrated aqua not only does not rust *clean* iron, but it actually prevents its rusting, even in the presence of water, oxygen, and ammonium carbonate. This conclusion indicates that *free* carbonic acid is necessary in the rusting of iron.

B. If iron, freshly rusted and still moist, be treated with concentrated aqua, the rusting continues for a considerable length of time. In this case we have iron coated, presumably, with more or less ferrous acid carbonate,  $\text{FeH}_2(\text{CO}_3)_2$ . This gives off free carbon dioxide and water in contact with the iron, and even in the strong aqua solution the rusting may be indefinitely continued by means of this very small amount of carbon dioxide.

C. Iron, which has been rusted for a considerable time, is not affected by concentrated aqua. The iron here is coated with ferric oxide and not ferrous acid carbonate, so there is no carbon dioxide available to cause further rusting.

The impurities to be found to a greater or less degree in aqua ammonia are carbon dioxide, tarry organic matter, pyridine, and seldom, if ever, hydrogen sulphide.

#### CARBON DIOXIDE.

The two methods which we have found to be best adapted for the determination of the small percentage of carbon dioxide in aqua are what may be termed the "precipitation" and the "direct titration method." The latter is the best, being the most accurate, as well as the most rapid.

*Precipitation Method.*—To 100 cc. aqua ammonia, in a suitable flask,<sup>1</sup> add 5 cc. normal sodium hydroxide,<sup>2</sup> and boil until the bulk of the solution is reduced to about 20 cc.<sup>3</sup> While still hot add 5 cc. barium chloride solution, drop by drop, and with constant shaking, filter immediately and quickly by suction, and wash the flask and filter five times, using about 10 cc. of water for each washing.<sup>4</sup> Return the precipitate and filter to the flask, add excess of fifth-normal sulphuric acid, boil to remove carbon

<sup>1</sup> A conical flask of about 300 cc. capacity is most convenient.

<sup>2</sup> The amount of carbon dioxide in 5 cc. of the normal sodium hydroxide must be determined and allowed for in the aqua analysis.

<sup>3</sup> By boiling down, all ammonia is removed, and all carbon dioxide retained as sodium carbonate.

<sup>4</sup> The object of the washing is to remove all traces of sodium hydroxide. The wash-water must be neutral and free from carbon dioxide, but should contain phenolphthalein, so as to carry out the removal of sodium hydroxide intelligently. The filter will still be slightly pink after washing five times, but this number has been found to give best results. Further washing dissolves barium carbonate and gives too low results.

dioxide and titrate back with fifth-normal sodium hydroxide, using phenolphthalein as an indicator.

$$1 \text{ cc. } N/5 \text{ NaOH} = 0.0044 \text{ gram CO}_2.$$

$$\text{No. of cc. } N/5 \text{ H}_2\text{SO}_4 - \text{cc. } N/5 \text{ NaOH} \times 0.044 = \text{grams per liter of CO}_2 \text{ in the aqua tested.}$$

The accuracy of this method was tested as follows :

I. 100 cc. of an aqua to which ammonium carbonate had been added was neutralized and the carbon dioxide present very carefully determined by absorption and weighing in the usual way.

Result: 100 cc. aqua contained 0.1253 gram carbon dioxide, which, for 25 cc. aqua would be 0.0313 gram carbon dioxide.

By the Precipitation Method.—(1) 25 cc. aqua contained 0.0315 gram carbon dioxide; (2) 25 cc. aqua contained 0.0317 gram carbon dioxide.

II. Tests by this method, omitting the evaporation of solutions containing a known amount of sodium carbonate, resulted as follows :

Carbon dioxide contained, gram.	Carbon dioxide found, gram.
0.0042	0.0042
0.0042	0.0044
0.0084	0.0079
0.0084	0.0081
0.0084	0.0092
0.0084	0.0088
0.0168	0.0169

III. Duplicate determinations, by this method, on 20 samples of aqua, have agreed in every case (with one exception) within 0.001 gram carbon dioxide per 100 cc. aqua.

*Direct Titration Method.*—1. To 100 cc. of the aqua, contained preferably in a 300 cc. conical flask, add 5 cc. normal sodium hydroxide and boil until the bulk of the solution is reduced to about 20 cc.

2. To this residue add 50 cc. of water (neutral, free from carbon dioxide and containing phenolphthalein), cool to 10° C., and bring to the neutral point by adding : first, normal sulphuric acid until the end point is nearly reached ; next, tenth-normal sulphuric acid until the last trace of pink is just removed. *Excess of sulphuric acid must not be present at any time during this neutralization.*

3. To the solution thus neutralized add a measured quantity of tenth-normal sulphuric acid (usually 10 cc.), boil two

minutes to remove carbon dioxide, cool, and titrate back with tenth-normal sodium hydroxide.

$$(\text{No. of cc. N/10 H}_2\text{SO}_4 - \text{cc. N/10 NaOH}) \times 0.044 = \text{grams per liter CO}_2 \text{ in the aqua.}$$

The carbon dioxide contained in 5 cc. normal sodium hydroxide must be determined and allowed for in the aqua analysis.

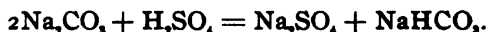
Concerning the respective steps of this analysis the following facts may be noted :

1. When aqua ammonia is boiled down in the presence of sodium hydroxide all carbon dioxide is retained as sodium carbonate, even though the evaporation be carried nearly to dryness. The purpose of boiling down with sodium hydroxide is to remove all ammonia, to reduce the bulk of the solution, and to retain all carbon dioxide as sodium carbonate.

2. The addition of acid as described, will set free a little carbon dioxide which may partially volatilize from the solution if the latter be too concentrated. By dilution with 50 cc. of water, this cause of error is averted.

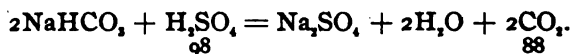
Before bringing to the neutral point the solution must be cooled to a low temperature (below 10° C.), otherwise the phenolphthalein color end point is not sufficiently distinct. Also there is less liability of loss of carbon dioxide by too rapid addition of acid, if the solution be well cooled.

The end-point is just reached when sufficient acid has been added to convert all the sodium carbonate into sodium bicarbonate, since the former is alkaline and the latter neutral to phenolphthalein. This neutralization is represented by the equation :



Excess of sulphuric acid must not be present at any time during this neutralization, because it will almost certainly cause a loss of carbon dioxide before excess of alkali can again be added.

3. The final step is the decomposition of the sodium bicarbonate by addition of an excess of sulphuric acid, the removal of carbon dioxide by boiling, and the titration of the excess of sulphuric acid by alkali.





One cc. tenth-normal sulphuric acid (0.0049 gram sulphuric acid) sets free 0.0044 gram carbon dioxide.

Hence :

$$(\text{No. of cc. N/10 H}_2\text{SO}_4 - \text{cc. N/10 NaOH}) \times 0.0044 = \text{grams CO}_2 \text{ in 100 cc. aqua.}$$

#### RESULTS.

#### TESTS WITH SODIUM CARBONATE SOLUTIONS CONTAINING A KNOWN AMOUNT OF CARBON DIOXIDE.

Carbon dioxide contained. Gram.	Carbon dioxide found by direct titration method. Gram.
0.0042	0.0042
	0.0080
	0.0085
	0.0087
0.0084	0.0078
	0.0080
	0.0085
	0.0080
0.0168	0.0166
	0.0161
	0.0164
0.0084	0.0088
	0.0086

The last two determinations were made at night, by the light of incandescent lamps.

A large number of determinations of carbon dioxide in aqua by this method, and a comparison of its results, on the same aquas, with those obtained by the precipitation method, have fully confirmed its accuracy.

#### CONCLUSIONS.

From the results obtained the conclusion is reached that the direct titration method for carbon dioxide in aqua ammonia is, all points considered, the best. It is accurate, rapid, and simple.

Equally accurate results can scarcely be obtained by the precipitation method, and the direct titration method requires less careful manipulation, takes less time, and avoids the liability to error which is occasioned by precipitation and washing of the barium carbonate. On the other hand in using the direct titration method, sulphides, if present, must be removed before making the titrations, while this removal is unnecessary in the case of the precipitation method.

Tarry organic matter, as found in ammonia, is best determined by oxidation with potassium bichromate instead of potassium permanganate, which in the cold does not completely oxidize, and at boiling temperature is itself decomposed, whereas potassium bichromate does not undergo decomposition, and with its use check results may be obtained even at different times of boiling. The method was devised by Mr. J. G. Hazard, and is the one we have adopted.

Potassium permanganate affects pyridine slightly, but by no means entirely oxidizes it. We therefore prefer to make a test for the organic matter with potassium bichromate which does not oxidize pyridine at all, and then make a separate determination of the pyridine. The method is as follows:

#### DETERMINATION OF ORGANIC MATTER IN AQUA AMMONIA.

Make up fiftieth-normal solutions of ammonium sulphate, ferrous sulphate, potassium permanganate, and potassium bichromate.

Introduce 10 cc. of aqua (from pipette) into a 300 cc. Erlenmeyer flask, add 20 cc. fiftieth-normal potassium bichromate solution (from burette), and 50 cc. dilute sulphuric acid (1 : 3). Heat to boiling and boil gently for about twenty minutes, adding distilled water if necessary to keep the volume above 50 cc. After boiling, cool to temperature of the room and add fiftieth-normal ammonium ferrous sulphate solution (from burette) in excess, and titrate back to faint pink color with fiftieth-normal potassium permanganate. The pink color will always fade out in a short time.

Add number of cubic centimeters potassium permanganate used, to number of cubic centimeters potassium bichromate used, and subtract number of cubic centimeters ammonium ferrous sulphate used. Deduct number of cubic centimeters potassium bichromate used up in a blank sample, and report result as number of cubic centimeters centinormal potassium bichromate used per 100 cc. aqua.

The end-point of the method appears to be perfectly definite, no further oxidation occurring by boiling considerably longer than the prescribed twenty minutes. The results obtained have indicated that all organic coloring-matter, or compounds which may change over into colored products are determined by this

method, while pyridine, and perhaps other stable organic bodies, are unattacked. A sample of aqua to which pure pyridine had been added gave almost exactly the same result as it gave by a test before the addition.

#### PYRIDINE.

Pyridine in aqua to be used in making liquid ammonia causes much trouble in the compressors and must be kept down to a low figure.

For the detection of traces of pyridine in commercial ammonia, "H. Ost recommends that the sample should be nearly neutralized when the odor of pyridine may be recognized. By distilling the nearly neutralized liquid, collecting the distillate in hydrochloric acid, evaporating, and extracting the residue with absolute alcohol, a solution is obtained containing but little ammonium chloride. What is present is removed by boiling off the alcohol and adding platinic chloride solution when, on evaporating the filtrate and adding alcohol, the pyridine chloroplatinate crystallizes in smooth, ramifying, orange-red prisms, readily soluble in boiling, but very sparingly in cold water."

But this is only a qualitative determination, while the following method gives excellent results quantitatively :

#### DETERMINATION OF PYRIDINE IN AQUA AMMONIA.

100 cc. of the aqua are nearly neutralized with sulphuric acid (1 : 5), keeping the mixture moderately cool meanwhile, so that pyridine will not be volatilized. Finally, cool to 20° C., add 1 or 2 drops of methyl orange and bring exactly to the neutral point with normal acid and alkali.

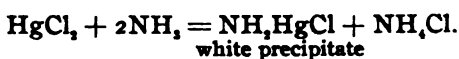
This neutral mixture is then placed in a suitable distilling flask and distilled until 70 cc. have passed over, the distillate being collected in 30 cc. of cold water contained in a small receiver.

Unless the aqua contains an unusually large amount of pyridine (*i. e.*, over 2.5 grams per liter), the 100 cc. of liquid now in the receiver contain *all the pyridine* which was present in the aqua and a small amount of free ammonia. The amount of ammonia ( $\text{NH}_3$ ) which is thus carried over will usually be equivalent to about 2 cc. normal solution.

Cool the contents of the receiver to below 10° C., add phenolphthalein, then, from a burette, mercuric chloride solution until

the last trace of pink is just removed, and finally 4 drops more of mercuric chloride solution to insure complete removal of the ammonia.

The mercuric chloride removes all the free ammonia according to the equation



Phenolphthalein is colored by free ammonia, but not by pyridine, so that the pink color of the solution is just removed when all the free ammonia has been acted upon.

The mixture is now filtered and the filtrate, containing pyridine bases alone, is titrated with normal sulphuric acid, after adding one drop of methyl orange for an indicator.

1 cc. normal  $\text{H}_2\text{SO}_4 = 0.079$  gram pyridine.

#### RESULTS OF DETERMINATIONS OF KNOWN QUANTITIES OF PYRIDINE IN AQUA.

Grams per liter present...	1.16	2.16	4.16	2.2	1.16
" " " found ....	1.11	2.0	4.11	2.3	1.15

Water, to which a known quantity of pyridine was added, was carried through the method.

Grams per liter present.....	1.9
" " " found.....	1.9

In the manufacture of aqua it is a great convenience to know, without making an analysis, the percentage of ammonia in an aqua by simply taking the degree Baumé. The temperature of the manufactured article as it leaves the absorber, of course, varies slightly.

Having determined the percentage of ammonia in three samples of different strengths, we have found the degree Baumé of each at temperatures varying from 10° C. to 30° C., and after plotting these on a chart, we have worked up the following table, by which, at a glance, one may learn the percentage of ammonia in a given sample of aqua, having determined the temperature and degree Baumé.

In shipping strong aqua, 29 to 30 per cent., to a hot climate in tank cars, one must take into consideration the great expansion of ammonia at temperatures which are likely to prevail in the summer months, and see to it that his tank will withstand the pressure as, of course, the tank will be sealed up. The following

PER CENT. OF AMMONIA IN AQUA FOR TEMPERATURES BETWEEN 10° C. AND 30° C., AND ANY DEGREE

BAUMÉ READING BETWEEN 24° AND 27°.

		COMMERCIAL AQUA AMMONIA.																						387
		10° C.	11° C.	12° C.	13° C.	14° C.	15° C.	16° C.	17° C.	18° C.	19° C.	20° C.	21° C.	22° C.	23° C.	24° C.	25° C.	26° C.	27° C.	28° C.	29° C.	30° C.		
Bé.	10° C.	26.2	26.0	25.8	25.7	25.5	25.3	25.1	24.9	24.8	24.6	24.4	24.3	24.1	23.9	23.7	23.6	23.4	23.3	23.1	22.9	22.8		
1	11° C.	4.2	4.2	4.2	4.2	4.2	4.2	4.2	4.2	4.2	4.2	4.2	4.2	4.2	4.2	4.2	4.2	4.2	4.2	4.2	4.2	4.2		
2	12° C.	6.4	6.4	6.4	6.4	6.4	6.4	6.4	6.4	6.4	6.4	6.4	6.4	6.4	6.4	6.4	6.4	6.4	6.4	6.4	6.4	6.4		
3	13° C.	8.6	8.6	8.6	8.6	8.6	8.6	8.6	8.6	8.6	8.6	8.6	8.6	8.6	8.6	8.6	8.6	8.6	8.6	8.6	8.6	8.6		
4	14° C.	10.8	10.8	10.8	10.8	10.8	10.8	10.8	10.8	10.8	10.8	10.8	10.8	10.8	10.8	10.8	10.8	10.8	10.8	10.8	10.8	10.8		
5	15° C.	13.0	13.0	13.0	13.0	13.0	13.0	13.0	13.0	13.0	13.0	13.0	13.0	13.0	13.0	13.0	13.0	13.0	13.0	13.0	13.0	13.0		
6	16° C.	15.2	15.2	15.2	15.2	15.2	15.2	15.2	15.2	15.2	15.2	15.2	15.2	15.2	15.2	15.2	15.2	15.2	15.2	15.2	15.2	15.2		
7	17° C.	17.4	17.4	17.4	17.4	17.4	17.4	17.4	17.4	17.4	17.4	17.4	17.4	17.4	17.4	17.4	17.4	17.4	17.4	17.4	17.4	17.4		
8	18° C.	19.6	19.6	19.6	19.6	19.6	19.6	19.6	19.6	19.6	19.6	19.6	19.6	19.6	19.6	19.6	19.6	19.6	19.6	19.6	19.6	19.6		
9	19° C.	21.8	21.8	21.8	21.8	21.8	21.8	21.8	21.8	21.8	21.8	21.8	21.8	21.8	21.8	21.8	21.8	21.8	21.8	21.8	21.8	21.8		
10	20° C.	24.0	24.0	24.0	24.0	24.0	24.0	24.0	24.0	24.0	24.0	24.0	24.0	24.0	24.0	24.0	24.0	24.0	24.0	24.0	24.0	24.0		
11	21° C.	26.2	26.2	26.2	26.2	26.2	26.2	26.2	26.2	26.2	26.2	26.2	26.2	26.2	26.2	26.2	26.2	26.2	26.2	26.2	26.2	26.2		
12	22° C.	28.4	28.4	28.4	28.4	28.4	28.4	28.4	28.4	28.4	28.4	28.4	28.4	28.4	28.4	28.4	28.4	28.4	28.4	28.4	28.4	28.4		
13	23° C.	30.6	30.6	30.6	30.6	30.6	30.6	30.6	30.6	30.6	30.6	30.6	30.6	30.6	30.6	30.6	30.6	30.6	30.6	30.6	30.6	30.6		
14	24° C.	32.8	32.8	32.8	32.8	32.8	32.8	32.8	32.8	32.8	32.8	32.8	32.8	32.8	32.8	32.8	32.8	32.8	32.8	32.8	32.8	32.8		
15	25° C.	35.0	35.0	35.0	35.0	35.0	35.0	35.0	35.0	35.0	35.0	35.0	35.0	35.0	35.0	35.0	35.0	35.0	35.0	35.0	35.0	35.0		
16	26° C.	37.2	37.2	37.2	37.2	37.2	37.2	37.2	37.2	37.2	37.2	37.2	37.2	37.2	37.2	37.2	37.2	37.2	37.2	37.2	37.2	37.2		
17	27° C.	39.4	39.4	39.4	39.4	39.4	39.4	39.4	39.4	39.4	39.4	39.4	39.4	39.4	39.4	39.4	39.4	39.4	39.4	39.4	39.4	39.4		
18	28° C.	41.6	41.6	41.6	41.6	41.6	41.6	41.6	41.6	41.6	41.6	41.6	41.6	41.6	41.6	41.6	41.6	41.6	41.6	41.6	41.6	41.6		
19	29° C.	43.8	43.8	43.8	43.8	43.8	43.8	43.8	43.8	43.8	43.8	43.8	43.8	43.8	43.8	43.8	43.8	43.8	43.8	43.8	43.8	43.8		
20	30° C.	46.0	46.0	46.0	46.0	46.0	46.0	46.0	46.0	46.0	46.0	46.0	46.0	46.0	46.0	46.0	46.0	46.0	46.0	46.0	46.0	46.0		

table shows the pressure developed by strong ammonia solutions exposed to different temperatures:

**PRESSURE PRODUCED BY EXPOSING AQUA AMMONIA TO DIFFERENT TEMPERATURES.**

The apparatus in which this test was made consisted of a cast-iron fitting piece with a pressure gauge and a mercury gauge attached. The relation of the liquor to the unoccupied space of the apparatus was the same as the relation of liquor in a tank car to the unoccupied space of the car. The apparatus was set in a water tank which was heated externally, and readings of the pressure gauge end of the mercury gauge made at every degree of temperature. The thermometer was placed in the aqua.

Experiment was carried to 120.2° F.

The rate of heating was 1° every six minutes.

The percentage of ammonia was 28.5, and the number of cubic centimeters aqua used was 2800.

°C.	°F.	Pounds pressure.	Inches mercury.	°C.	°F.	Pounds pressure.	Inches mercury.
23	73.4	2½	4½	37	98.6	10½	21¾
24	75.2	3	6½	38	100.4	11	22¾
25	77.0	4	7½	39	102.2	11½	23¾
26	78.2	4½	8¾	40	104	12	24¾
27	80.6	5	9¾	41	105.8	12½	25½
28	82.4	5	10¾	42	107.6	13	26¾
29	84.2	5	11¾	43	109.4	13½	27¾
30	86	6	12¾	44	111.2	14	28¾
31	87.8	6½	13¾	45	113	14½	29¾
32	89.6	8	16	46	114.8	15	30¾
33	91.4	8	17¾	47	116.6	15½	31¾
34	93.2	9	18¾	48	118.4	16	32¾
35	95	9½	19	49	120.2	16½	33¾
36	96.8	10	20½				

**A NITROGEN APPARATUS.**

By J. A. WESENER.

Received November 20, 1901.

THE purpose of this apparatus, as illustrated and described herewith in detail, is to secure greater rapidity in the ordinary nitrogen estimation. The method adopted in this apparatus for estimating nitrogen is by distilling the alkaline mixture in a current of steam, using the same steam which makes the

distilled water in the laboratory. This apparatus has been in constant use in the Columbus Laboratories since last March.

In point of accuracy, it is equal to the common prevailing method, while in rapidity it by far outclasses the old method. Ten minutes from the time the jet of steam is turned on is amply sufficient to expel all the ammonia in the product digested according to the official Kjeldahl method, and obtaining 250 cc. distillate in each flask.

The general description of the apparatus is as follows: The distillation flask is round-bottomed, and of 24 ounce capacity. In the neck of this flask is fitted a perforated rubber stopper, and flush with both ends a copper tube. To the upper end of this tube is fitted two hollow brass balls, the first and smallest being of about 40 cc., and the largest of 70 cc. capacity. Entering at the top of the first ball, and passing nearly to the bottom of the flask, is a thistle tube of glass, with a stop-cock. The object of this tube is to allow the alkali to be put in after the flask is connected with the condenser, and hence no ammonia is lost while connecting the apparatus.

From the side of the brass ball nearest the condenser leads a pipe of block tin tubing curving up to the second brass ball, which, as stated, is larger than the first. From this second ball a block tin tube leads again to the condensing coil, and is soldered in place at both ends. On the side of the first brass ball farthest from the condenser, at the junction of the ball with the tube, leading through the rubber stopper, is a small brass tube,  $\frac{1}{16}$  of an inch in diameter, with the joint at right angles, and joined to this is a glass tube which passes down below the surface of the liquid in the flask. Through this tube passes the steam for distillation. In the operation of the original apparatus, the steam is furnished from a boiler heated by steam coils, which is the source of the laboratory's distilled water.

In the apparatus as above described the operation is carried on as follows: The material is digested in a 24-ounce, round-bottomed flask, by using 15 cc. of concentrated sulphuric acid, plus a globule of mercury. After the digestion is complete, the flask is allowed to cool; is then diluted with distilled water, and connected to the apparatus. Sixty cc., which is the amount the cup in the thistle tube will hold, of 50 per cent. strength sodium hydroxide, is next added, the steam turned on, so as to mix the

alkali and acid, and then 20 cc. of the 4 per cent. potassium sulphide solution is added. The object of adding the potassium sulphide solution last is to avoid carrying over hydrogen sulphide in the distillate. The distillate is collected in ordinary 500 cc. flasks, in which a little distilled water is placed, so as to dilute the ammonia as it distils off.



I have found that no ammonia is lost by simply allowing the distillate to run in a flask containing distilled water, and therefore dispense with using standard acid solution. A trial of six ureas were digested according to the Kjeldahl method; three of the distillates were collected in decinormal sulphuric acid solution, and the other three were collected in distilled water, all titrated the same.

The steam pressure necessary to run a battery of six flasks briskly is 1 to 2 pounds. In case no steam is available in the laboratory, then a small copper boiler can be used, which being heated with one large gas-burner will furnish sufficient steam to run 6 flasks.

#### GOOD POINTS ABOUT THIS APPARATUS.

1. The material is digested in a 24-ounce round-bottomed flask, and therefore requires no transferring.
2. The operation is rapid. One 6-battery apparatus (which is the one illustrated) will make from 80 to 100 nitrogen distillations daily. The apparatus can be made up in duets, quartets, sextets, or any number desired.
3. No glass joints and rubber tubing, therefore no leaking.
4. Large saving of gas and time.
5. Economy of space. The 6-battery apparatus, when set up ready for use, requires a space of 24 by 24 inches only.
6. The apparatus can be run with one, two, or any number of the batteries up to the limit. Each battery being independent of the other, if one determination is completed before the others, it can be recharged without any interruption to the rest of the apparatus.
7. The apparatus can be used for water analysis, in which case the solution is boiled in the flask either by gas flame or with steam, which has been purified from ammonia. This purification can be accomplished by the addition of sulphuric acid and potassium permanganate.



## A NEW FORM OF ALKALIMETER.

BY CHARLES B. DAVIS.

Received February 3, 1900.

THE apparatus (Fig. 1) may be described as follows: A (Fig. 2, I) is the water or acid chamber of about 10 cc. capacity, to the bottom of which is attached a bent capillary tube for the passage of the water or acid to the body of the apparatus. The liquid in this chamber is held in place by virtue of the existing pressure below and partial vacuum above the liquid, there being no stop-cocks to get out of order. B is the drying chamber which is supplied with two bent capillary tubes for the introduction of the gas into the drying material, which is generally concentrated sulphuric acid. Both chambers are supplied with



Fig. 1.

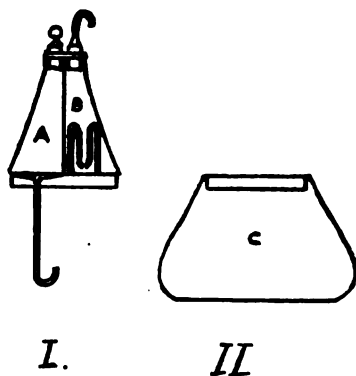


Fig. 2.

glass stoppers, and are separated by a glass partition. C (Fig. 2, II) is the body of the alkalimeter having a capacity of about 75 cc., which is intended to carry the material to be tested. The convenience of this section of the apparatus is that it may be tared on the balance, and a portion of the sample to be examined weighed directly into the alkalimeter, thus avoiding all loss caused by transferring, as in the average alkalimeter now in use. I and II are connected by an air-tight ground joint.

The alkalimeter having been thoroughly cleansed and dried, the body of the apparatus is tared, and a portion of the material to be examined, in powdered form (which should contain not more than 0.5 gram of carbonate), is weighed in together with 2 grams of a mixture of equal parts salicylic and benzoic acids.

The mixed acids I have found to give better results for all carbonates, than either alone, although either will answer the purpose in most cases.

The drying chamber is half filled with concentrated sulphuric acid, and to the water chamber is added 10 cc. distilled water freed of the gases it usually contains. Both sections are now brought together and allowed to attain the temperature of the balance.

The alkalimeter thus charged is carefully tared, and by removing both stoppers the water flows into the body of the apparatus, which causes an immediate generation of carbon dioxide; this moisture-laden gas passes through the capillary tubes into the acid of the drying chamber where it is deprived of its moisture and escapes. When this first evolution of gas ceases, the apparatus is carefully shaken, and this is repeated until no further generation of gas results. No heat is employed for the alkaline carbonates, while for the earthy carbonates a temperature as low as 55° will be found to be sufficient.

The alkalimeter is now freed of its remaining carbon dioxide by causing 0.5 liter of dry air, freed from carbon dioxide, to pass through the apparatus.

The following results were obtained with calcium, barium, and magnesium carbonates:

#### CARBON DIOXIDE.

	Found.	Theory.
Calcium carbonate.....	43.98	44.00
Barium carbonate.....	22.38	22.33
Magnesium carbonate.....	52.40	52.38

This method for estimating carbon dioxide will be found useful in the examination of baking-powders, as well as for the alkaline and earthy carbonates.

### THE DETERMINATION OF LITHIA IN LEPIDOLITE.

BY W. J. SCHIEFFELIN AND W. R. LAMAR.

Received February 3, 1908.

THE J. Lawrence Smith method for decomposing the silicate is more convenient than that of dissolving in hydrofluoric acid, as the alkalis are separated from the alumina as chlorides in one step, thus avoiding two precipitates, aluminum hydroxide and barium sulphate, which are sure to hold back lithia. A

modification we have found advisable, is to remove the last traces of calcium by means of ammonium oxalate.<sup>1</sup> The Gooch method<sup>2</sup> for separating lithia from the other alkalies gives the best results. A small direct vision spectroscope is an important aid in deciding when precipitates are thoroughly washed, etc., by examining a fraction of a drop held in a looped platinum wire.

The decomposition is conducted in the usual way,<sup>3</sup> care being taken that the crucible is not heated too highly, as there is danger of loss of the lithium chloride, and also of the mass becoming vitrified and difficult to dissolve.

The trituration must be thorough and the leaching complete or some lithia will be held back. (The residue when treated with hydrochloric acid should leave no undecomposed mineral.)

After the dish containing the alkalies is dry, it is heated on an asbestos disk, or a triangle high above the flame, to drive off the ammonium chloride; this may take three-quarters of an hour; if it is done too rapidly, lithium chloride will go with it.

Ten cc. of hot water and one drop of hydrochloric acid will dissolve the residue in the dish, and the addition of a few drops of ammonia, and 1 or 2 drops of ammonium oxalate precipitate the remaining calcium.<sup>4</sup>

The chlorides of the alkalies are filtered into an Erlenmeyer flask, of thin glass (75 or 85 cc. capacity), which is placed in the air-bath, or on an asbestos disk over a small flame, and evaporated until the salts show signs of crystallizing (the solution will be down to 1 or 2 cc.); then a few drops of water are added, to effect solution, and 1 or 2 drops of concentrated hydrochloric acid to transform any hydroxide or oxychloride into chloride. Fifteen cc. of amyl alcohol (b. p. 129°–132° C.) are now added, and the flask is placed on an asbestos disk, which is slightly slanted so that the lower aqueous layer flows to one side, and the point of a Bunsen flame (1.5 inches high) is applied to the asbestos directly under the raised side of the flask. It is important to adopt this precaution as it allows the amyl alcohol to come to gentle boiling and continue boiling after all watery vapor

<sup>1</sup> Hillebrand: *Bull. U. S. Geol. Survey*, No. 176.

<sup>2</sup> *U. S. Geol. Survey Bull.* No. 42, p. 73; *Am. Chem. J.*, 9, 33; *Proc. Am. Acad.*, p. 177 (1886); *Chem. News*, 88, 18, 29, 40, 56, 78.

<sup>3</sup> Fresenius, § 140.

<sup>4</sup> Hillebrand: *U. S. Geol. Survey, Bull.* No. 176.

has gone off, without the tendency to bumping which causes inevitable loss.

Boiling the amyl alcohol is continued until half has evaporated. Toward the end the flame may be slightly raised and it is well to hold a thermometer in the vapor; it should read  $129^{\circ}$ – $130^{\circ}$  C., showing that the water has been driven off.

The amount of amyl alcohol remaining for the Gooch correction is judged by adding water to a flask of the same size to the same level and measuring the water.

The amyl alcohol is decanted when cold through a small filter into a weighed platinum dish; the filter is first moistened with anhydrous amyl alcohol and the residue in the flask and the filter are carefully washed with the same until free from lithia. This will require 20 cc.

The amyl alcohol is expelled from the platinum dish in a hot air-bath, under the hood, at a temperature not higher than  $125^{\circ}$  C. At this temperature it rapidly evaporates but does not boil or spatter.

After complete dryness, 0.5 cc. of concentrated sulphuric acid is added to the dish, which is warmed and rotated until all the residue has been moistened and all the chloride decomposed, and the excess of sulphuric acid is now carefully driven off by heating over a small flame or by rotating over a moderate flame. Haste in doing this will cause loss.

The lithium sulphate in the platinum dish is ignited to burn off all carbon left by the amyl alcohol, which takes but a few moments. The sulphate fuses and is kept one minute in fusion, then the dish is allowed to partially cool and covered with a watch-glass or filter-paper, to return any fragments of the fused sulphate, which sometimes splits off when it contracts.

The dish is then cooled in a desiccator and weighed; after fusing again the weight is usually found to be constant. The deduction for sodium and potassium is made as directed by Gooch.<sup>1</sup> That rubidium and caesium chlorides are virtually insoluble in amyl alcohol is shown by the following:

0.1022 gram rubidium chloride dissolved in water, with a drop of concentrated hydrochloric acid, treated as in the analysis with 15 cc. amyl alcohol and boiled down to 9 cc., left 0.0009 gram

<sup>1</sup> Deduct 0.0011 gram for each 10 cc. amyl alcohol exclusive of washings.

residual sulphates, which showed sodium strongly, also potassium, lithium and rubidium in the spectroscope.

0.1037 gram caesium chloride in the same way, with the amyl alcohol boiled down to 7 cc., left 0.001 gram residual sulphates, showing sodium, lithium, caesium, and potassium.

If the sulphate in the dish is pure, it dissolves readily in a small amount of hot water and gives a good lithium flame. To prove that the sulphate residue obtained in the analysis was lithium sulphate, the following parallel was made: An equivalent weight of pure lithium carbonate (99 per cent.) was weighed into a second platinum dish, transformed into sulphate, ignited, weighed and the lithia in both dishes determined as phosphate as directed in Fresenius, using exactly the same amounts of sodium phosphate, sodium hydroxide and ammonia wash-water, and collecting the precipitates but twice.

	Lithium sulphate. Gram.	Lithium phosphate obtained. Gram.	Lithium phosphate calculated. Gram.
A. From analysis .....	0.1020	0.0706	0.0717
B. From carbonate.....	0.1004	0.0670	0.0705

It will be seen that there are a number of precautions to be observed in order to avoid loss of lithia, either by leaving it behind, driving it off, or mechanically carrying it off. Good results will, however, be obtained, if care is taken to use a low red heat in the fusion; to thoroughly leach and triturate the fused mass; to avoid high heat in driving off the ammonium chloride; to avoid bumping when boiling the water out of the amyl alcohol; to filter the amyl alcohol cold; to evaporate the amyl alcohol in the dish at a temperature below its boiling-point; to drive off the sulphuric acid without any foaming or boiling; and to cover the dish while the lithium sulphate is cooling.

The analysis can be completed in two days.

LABORATORY OF SCHIEFFELIN & Co.  
November 22, 1901.

[CONTRIBUTION FROM THE BUREAU OF CHEMISTRY, U. S. DEPARTMENT OF AGRICULTURE, No. 43. SENT BY H. W. WILEY.]

## A NOTE ON THE USE OF THE BECHI OR SILVER NITRATE TEST ON OLIVE OILS.

By L. M. TOLMAN.

Received January 20, 1902.

THE author, in working with a large number of salad oils, found that nearly all of them gave a brown coloration with the Bechi test, as ordinarily applied, unless the sample was first purified as described below. The modification of the reagent used was that proposed by Pearman and Moor,<sup>1</sup> and later by Wesson.<sup>2</sup>

Two grams of silver nitrate are dissolved in 200 cc. of 95 per cent. alcohol, to which 40 cc. of ether and two drops of nitric acid are added. Ten cc. of oil, 10 cc. of amyl alcohol, and 5 cc. of the reagent are mixed in a test-tube.<sup>3</sup> Half the mixture is poured into another test-tube and kept for comparison. The other half is heated for ten minutes in a boiling water-bath and compared with the unheated portion. The brown coloration and reduced silver show the presence of cottonseed oil. Treated in this way, some oils which were especially rancid gave a strong test with the Bechi reagent, but from the physical and chemical constants and the Halphen reaction cottonseed oil could not have been present.

It has been advised to heat the oil for one hour at 100°, but this, while it reduced the reaction of the reagent with other oils, also weakened the reaction with cottonseed oil and was not at all satisfactory.

Wesson advises treatment with 2 per cent. nitric acid, but while this purified the oil in some cases it could not be depended on always, since quite a number of the oils treated in this way gave strong reactions although they contained no cottonseed oil.

The use of a dilute alkali works very well but is inconvenient, for it emulsifies and separates very slowly. A method which is much easier, more rapid, and one which gives very satisfactory results is as follows:

To about 25 cc. of the oil add 25 cc. of 95 per cent. alcohol,

<sup>1</sup> Allen's "Commercial Organic Analysis," Vol. II, Part I, second edition, p. 143.

<sup>2</sup> This Journal, 17, 724.

<sup>3</sup> Amyl alcohol is used to dissolve the fats or oils and thus secure a much better mixture with the reagent.

heat gently, and shake vigorously; allow to stand until the liquids separate, decant as much of the alcohol solution as possible, and then wash the residue with 2 per cent. nitric acid and finally with water. Cottonseed oils treated in this manner reacted with undiminished strength, while the olive oils which before treatment gave deep brown colorations, showed after treatment no coloration or reduction of the silver solution at all. The free fatty acids and other products of rancidity, which are evidently the cause of the brown coloration with the Bechi reagent which these oils give, are dissolved by the alcohol and removed while the reducing principle of the cottonseed oil is not affected. This method can be readily applied to lards or other fats which it is desirable to test by the Bechi reagent. The writer was able, by this method, to get very satisfactory and reliable results.

## A STUDY OF THE BECHI TEST FOR COTTONSEED OIL.

BY AUGUSTUS H. GILL AND CHARLES H. DENNISON.

Received February 3, 1908.

WHILE in the case of sesame oil the substances to which the Baudouin test is due may be said to be fairly well known,<sup>1</sup> such is not the case with the test in question. Some<sup>2</sup> consider that it is due to a sulphur compound in the oil and others<sup>3</sup> to an aldehydic body. While the evidence given by this paper is not conclusive, it was thought sufficiently interesting to publish.

The tests made by these various experimenters were repeated and confirmed; it was found that an oil heated to 260° gave neither the Bechi-Milliau test nor the Halphen test. This might indicate that the active principle of both tests was the same but for the fact that Raikow,<sup>4</sup> by oxidizing the oil with potassium permanganate and sulphuric acid, obtained an oil which gave the Bechi test but not the Halphen.

### TESTS FOR ALDEHYDIC BODIES.

400 cc. of oil were shaken with an equal quantity of strong sodium bisulphite solution for twelve hours; the oil upon separation gave the Bechi test although a longer time was required for

<sup>1</sup> Villavecchia and Fabris: *Abstr. J. Soc. Chem. Ind.*, 16, 1045.

<sup>2</sup> Dupont: *Bull. Soc. Chim.*, 13, 696; Charabot and March: *Ibid.*, 21, 552.

<sup>3</sup> Holde: *J. Soc. Chem. Ind.*, 11, 637; Wilson: *Chem. News*, 89, 99.

<sup>4</sup> *Chem. Ztg.*, 24, 562, 583.

its development and it appeared in less intensity. This was repeated with similar results; in this latter case crystals separated, which on being distilled with sodium carbonate gave no aldehyde reaction with the fuchsine-aldehyde reagent.

A portion of the oil was treated with dry ammonia gas for seven hours; there was no indication of any crystalline compound of aldehyde ammonia having been formed, and the oil gave the Bechi-Milliau test with even greater intensity.

#### TEST FOR SULPHUR COMPOUNDS.

In two cases only the black compound formed by the action of silver nitrate upon the fatty acid gave off hydrogen sulphide; this was recognized by its odor and blackening lead acetate paper. If, however, sulphur compounds were present in the fatty acid sufficient to blacken silver nitrate, it would seem as if other metallic salts should show characteristic colors. Salts of cadmium, lead, copper, and mercury were tried with negative results except that with the mercury salts reduction to metallic mercury took place.

In the repetition of Dupont's work both the aqueous distillate from the unheated oil and the oil itself gave the Bechi test. This was not the case with the oil which had been heated to  $260^{\circ}$ . In conclusion, in view of the fact that bodies of an aldehydic character could not be detected in the oil by either the fuchsine aldehyde reagent, by sodium bisulphite, or by ammonia, it would seem that it was not likely that they were present. This would seem to be confirmed by Raikow's oxidation with permanganate and sulphuric acid. The evidence would seem to favor the presence of sulphur compounds.

---

#### NEW BOOKS.

STUDIES FROM THE CHEMICAL LABORATORY OF SHEFFIELD SCIENTIFIC SCHOOL. EDITED BY HORACE L. WELLS. Vol. I, xi + 444 pp. Vol. II, ix + 379 pp. New York: Charles Scribner's Sons. 1901. Price, \$7.50 per set.

In consequence of the recent bicentennial celebration of Yale University, there has been presented to the world "a series of volumes \* \* \* prepared \* \* \* and issued \* \* \* as a partial indication of the character of the studies in which the University teachers are engaged." Two volumes of this series.



bearing the title given in the head lines, have been placed in the hands of the writer, who has read them with the greatest pleasure. The first volume contains a brief sketch of the Sheffield Laboratory, including a list of the publications (131) of the present officials of the department and their collaborators, followed by a series of papers in detail relating to general inorganic chemistry. Although the writer had studied these investigations as they appeared in print in the various journals, he can truthfully say that from the moment his attention was again attracted to the first lines of the first article which read "in the course of some experiments with caesium compounds, bromine was added to a concentrated solution of caesium chloride with an astonishing result," his interest in the remarkable results obtained in the preparation and study of double halides, by Professor Wells and his associates, was revived; indeed, this interest became so great that he read on and on, through one paper after the other, unconscious of his surroundings and the flight of time until the final paragraph was reached, when the book was closed with the conviction that it was overflowing with facts, bristling with suggestions, and deserving of the most careful study by all chemists, but especially those who fail to realize the immense work remaining to be done in the inorganic field. Five hundred double halides have been studied, more than a third of which have been made in the Yale laboratory. It is not very surprising then to read in the final chapter, "that the valency of a negative halide has no influence upon the types of double salts that it forms;" that "molecules of alkaline halides possess nearly the same combining power as negative halides; that double halides probably increase in ease of formation and variety from the iodides to the fluorides," and then "some indications of regularity have been observed in connection with these researches, but it must be admitted that the results have been negative as far as throwing light upon the structure of this class of compounds is concerned."

While the prevailing thought in Volume I is "double halogen salts," we meet in the companion volume anilides, formyl derivatives, amidines, imido esters, thiazoles, urea amidines, acyclic benzoyl pseudoureas and thiosemicarbazidic esters—all attesting, by the skilful way in which they have been prepared and studied, the keen originating power, and the untiring energy and zeal of their various authors. Just a bit of the "double halide" spirit

has found its way into several of these organic papers, for upon p. 34 will be noticed



which are perfectly analogous to the perhalides  $\text{CsBr.Br.}$ ,  $\text{CsI.I.}$ , and  $\text{NH}_4\text{Br.Br.}$ . This slight digression into the field that received such ample consideration in the first volume is most pardonable, nay, it is desirable and should be pursued farther whenever it is at all possible. Much more might be said, but as the character of the volumes is now in a measure indicated, the writer would conclude with the recommendation that the reader of these lines should study the papers for himself, feeling assured that when he has done so, he will concur with the writer in the opinion that these researches not only reflect great credit upon their authors and the university in which they were planned, but that they will be real incentives to the great body of young, enthusiastic chemists to go forward and do likewise.

EDGAR F. SMITH.

## THE JOURNAL

OF THE

## AMERICAN CHEMICAL SOCIETY.

CONTRIBUTIONS TO THE CHEMISTRY OF THE RARE  
EARTHS OF THE YTTRIUM GROUP. I.

BY L. M. DENNIS AND BENTON DALES.

Received January 30, 1902.

## HISTORICAL.

THE first of the rare earths was discovered by Gadolin,<sup>1</sup> in 1794, in a heavy black mineral which had been found at Ytterby some six years before by Arrhenius. Three years later the earth was named yttria by Ekeberg,<sup>2</sup> and the mineral "yttria-stone." The latter is the gadolinite of the present day mineralogists. Ekeberg<sup>3</sup> found yttria in a new mineral in which he had discovered tantalum and which he called yttrotantalite. The earth was further studied by Berzelius<sup>4</sup> and by Berlin,<sup>5</sup> both of whom considered it homogeneous.

Scheerer<sup>6</sup> observed that when yttria was heated strongly in an open vessel it took on a yellow color, which it lost on heating in the presence of reducing gases, and that it remained colorless if cooled quickly, whereas it became colored again if heated in contact with air. He thought this phenomenon due to the presence

<sup>1</sup> Sv. Vet. Akad. Handl., p. 137 (1794); Crell's *Ann.*, (1796) I, 313.

<sup>2</sup> Crell's *Ann.*, 2, 63 (1799).

<sup>3</sup> Sv. Vet. Akad. Handl., p. 68 (1802); *Ann. de Chim.*, 43, 278.

<sup>4</sup> *Schw. J.*, 16, 404.

<sup>5</sup> Sv. Vet. Akad. Handl., pp. 209, 212 (1835); *Ann. Chem.* (Liebig), 28, 222.

<sup>6</sup> *Pogg. Ann.*, 56, 482.

in the yttria of some other earth, perhaps new, perhaps lanthana, capable of forming easily a peroxide. His work was soon followed by the researches of Mosander,<sup>1</sup> who separated the old yttria into three new earths. He kept the name yttria for the most basic of these; the middle one he called terbia and the least basic one erbia. His yttria was white and gave colorless salts; terbia he thought to be white also, but it gave rose-colored salts, while erbia was orange-yellow and gave colorless salts. He used the methods of fractional precipitation of the oxalates by oxalic acid from acid solution, and of the hydroxides by dilute ammonia, in both of which his erbia was thrown out first, then terbia and lastly yttria. His results were confirmed by Berzelius<sup>2</sup>, by Svanberg, and by Scheerer.

The earths of old yttria were reexamined in 1860 by Berlin.<sup>3</sup> He was the first to use the classic method of fractional decomposition of the nitrates by heat. He obtained only two of Mosander's earths, the white yttria and the one giving rose-colored salts, terbia, which he and all subsequent investigators have called erbia. Mosander's yellow erbia, the present-day terbia, he could not obtain.

Popp<sup>4</sup> in 1864, and Delafontaine<sup>5</sup> in that year and the two following ones, working at this same problem, arrived at totally different conclusions. Popp, using both of Mosander's methods, could separate neither erbia nor terbia. He thought erbia a mixture of the cerite oxides, and terbia a mixture of erbia with yttria. Delafontaine maintained that these two earths existed. Mosander's erbia he obtained by fractional precipitation with primary potassium oxalate, the small amount of yttria and terbia being removed by treatment with potassium sulphate solution. To separate the terbia and yttria remaining, he fractioned again the least-colored oxalates, then dissolved out the yttria by repeated treatment with dilute acid.

Then Bahr and Bunsen<sup>6</sup> in 1866, using a modification of Berlin's method of fusion of the nitrates, corroborated Berlin's results. They obtained only the true or white yttria and the rose-colored

<sup>1</sup> *Phil. Mag.*, 23, 251; *Ann. Chem. (Liebig)*, 48, 219.

<sup>2</sup> "Lehrbuch," 2nd French Edition, 2, 163.

<sup>3</sup> *Scand. Naturf. 8 Møde Kjöbenhavn*, p. 448 (1860).

<sup>4</sup> *Ann. Chem. (Liebig)*, 131, 179.

<sup>5</sup> *Arch. des Sci. phys. et nat.*, (2) 21, 97; 22, 30; 23, 105; *Ann. Chem. (Liebig)*, 134, 99; 135, 188.

<sup>6</sup> *Ann. Chem. (Liebig)*, 137, 1.

erbia of Berlin (Mosander's terbia). Cleve and Höglund<sup>1</sup> in 1872, using the same method, obtained the same result.

Until Mendeléeff's announcement of the periodicity of the elements,<sup>2</sup> yttria, ceria and the other rare earths had been generally assumed to have the formula RO. He, however, showed that their properties placed them in the third group of his arrangement, where their maximum valence would be three (oxide,  $R_2O_3$ ). Lanthana he considered to be  $RO_2$ . In order to put them into this group, it was necessary to increase their accepted atomic weights by one-half. Cleve<sup>3</sup> in 1874, published new researches upon the salts of yttria and erbia, which tended to show the correctness of Mendeléeff's view of the triatomicity of these earths. Nilson,<sup>4</sup> working upon the selenites in 1875, and upon the chlor-platinum compounds in 1876, further strengthened the idea that the rare earths, lanthana included, were sesquioxides.

A great increase in activity in rare earth research occurred in 1878, when the mineral samarskite, found in large quantities in North America, became the source of the material.

Smith<sup>5</sup> in 1877 isolated an earth which he considered to be new, or perhaps the third earth of Mosander. He thought it new because of the insolubility of its double potassium sulphate in saturated potassium sulphate solution. Marignac<sup>6</sup> showed this property to be only a relative one, and he deemed Smith's mosandria to be identical with terbia. Neither could he agree to Smith's other claim that mosandria was identical with Soret's X. Delafontaine<sup>7</sup> considered mosandria to be terbia. Considerably later (1886), Lecoq de Boisbaudran,<sup>8</sup> having obtained a sample of Smith's impure mosandria, found that it contained, besides didymia and samaria, gadolinia and terbia.

Delafontaine<sup>9</sup> and Marignac<sup>10</sup> settled the question as to the existence of terbia by preparing it. Delafontaine treated his yttria earth mixture in solution with a saturated solution of sodium sulphate containing crystals of the salt, then fractioned the pre-

<sup>1</sup> *Bull. Soc. Chim.*, (2), 18, 193, 289.

<sup>2</sup> *Ann. Chem.* (Liebig), Suppl., 8, 133, esp. p. 184 ff.

<sup>3</sup> *Bull. Soc. Chim.*, (2), 21, 344.

<sup>4</sup> *Ber. d. chem. Ges.*, 8, 655; 9, 1056, 1142.

<sup>5</sup> *Proc. Acad. Nat. Sci., Phila.*, 29, 194; *Compt. rend.*, 87, 146, 148.

<sup>6</sup> *Arch. des Sci. phys. et nat.*, (2), 63, 172; *Compt. rend.*, 87, 281.

<sup>7</sup> *Compt. rend.*, 87, 600.

<sup>8</sup> *Loc. cit.*, 102, 647.

<sup>9</sup> *Arch. des Sci. phys. et nat.*, (2), 61, 273; *Ann. chim. phys.*, (5), 14, 238.

<sup>10</sup> *Arch. des Sci. phys. et nat.*, (2), 61, 283; *Ann. chim. phys.*, (5), 14, 247.

precipitated portion with oxalic acid from strong nitric acid solution, and finally treated the first of these precipitates with formic acid and concentrated. Terbia crystallized out as formate. There was also a yellow earth in the portion soluble in the sodium sulphate, but it was not so deeply colored as terbia and gave besides a base of lower atomic weight. He thought it a new element. Marignac obtained terbia as well as yttria and erbia by fusion of the nitrates. By making several hundred fractions and by properly combining them he obtained finally pure yttria at one end and erbia at the other. The intermediate products possessed a yellow color. These he combined and fractioned by oxalic acid in acid solution. Erbia and didymia he found to go with terbia. Didymia he removed by the potassium sulphate treatment, but he could not free his product from erbia. Hofmann and Krüss<sup>1</sup> in 1893 studied terbia, and by fractionation with aniline hydrochloride succeeded in breaking it up into two probable earths with metal atomic weights of 148 to 150 and 160, calculated as  $R^{III}$ . In 1895 Lecoq de Boisbaudran<sup>2</sup> called attention to an absorption band in his terbia material which could not belong to any known element. He called the one which gives it  $Z_d$ . Its band was at  $\lambda 487.7$ .

The new earth which Delafontaine suspected in the saturated sodium sulphate solution mentioned above, was announced by him<sup>3</sup> as philippia. It was characterized by a magnificent absorption band in the violet at  $\lambda 450$ . Soret<sup>4</sup> stated that philippia was identical with the earth X, which Cleve<sup>5</sup> denied. Delafontaine<sup>6</sup> maintained that philippia, Soret's X, and Cleve's holmia were identical, which Cleve again denied. Delafontaine<sup>7</sup> then admitted that the absorption spectrum ascribed by him to philippia belonged to Soret's X, but maintained still the individuality of the former. Roscoe,<sup>8</sup> in 1882, by fractional precipitation of the double potassium sulphates with potassium sulphate, and by fractionation of the first portions of these by the varying solubilities of the formates, could obtain no product whose metal had

<sup>1</sup> *Ztschr. anorg. Chem.*, 4, 27.

<sup>2</sup> *Compt. rend.*, 121, 709.

<sup>3</sup> *Loc. cit.*, 87, 559.

<sup>4</sup> *Loc. cit.*, 89, 521.

<sup>5</sup> *Loc. cit.*, 89, 708.

<sup>6</sup> *Loc. cit.*, 90, 221.

<sup>7</sup> *Arch. des Sci. Phys. et nat.*, (3), 3, 246.

<sup>8</sup> *Ber. d. chem. Ges.*, 15, 1274.

a constant atomic weight of 121 to 123, and he concluded that philippia was a mixture of terbia and yttria. Crookes<sup>1</sup> agreed with Roscoe as to the non-existence of philippia. In 1897, Delafontaine<sup>2</sup> gave the methods by which philippia might be prepared; they were the standard ones of fractional precipitation of the nitrate solution of the rare earths with ammonia, or with primary potassium oxalate, or fractional decomposition of the nitrates by heat. Urbain,<sup>3</sup> in 1900, denied the existence of philippia.

In this year of 1878, while studying the impure didymia from samarskite, Delafontaine<sup>4</sup> discovered a new oxide which he called decipia. Its metal had a high atomic weight ( $R^{III} = 159$ ), and it was characterized by the absorption bands  $\lambda_{416}$  and  $\lambda_{478}$ . Lecoq de Boisbaudran<sup>5</sup> found, in a spectroscopic examination of a mixture of earths rich in didymia from samarskite, some new rays. In the spark spectrum there were four rays: in the absorption spectrum, two strong bands and three faint ones. The strong bands were in the blue and had their centers at  $\lambda_{480}$  and  $\lambda_{463.5}$ . One of the other bands had a wave-length of  $\lambda_{416}$ , which had been ascribed by Delafontaine to one of the bands of decipia. Lecoq de Boisbaudran finally separated the earth giving these bands from didymia, and he called it samaria. Then Marignac,<sup>6</sup> by fusion of the nitrates and fractionation of the double potassium sulphates, isolated two earths which he called  $Y_a$  and  $Y_b$ . The double potassium sulphate of  $Y_a$  was comparatively soluble in potassium sulphate solution; solutions of the earth gave no absorption spectrum, and the equivalent weight of the metal was about 120.5 (RO).  $Y_b$ , on the other hand, gave a double potassium sulphate less soluble in potassium sulphate solution; solutions of the earth gave an absorption spectrum corresponding to that of decipia or better to that of samaria, and the metal had an equivalent weight of 115.6.  $Y_a$  has since been called gadolinium.<sup>7</sup> Delafontaine<sup>8</sup> again in 1881 showed that, by treating those earth sodium double sulphates most insoluble in a saturated solution of Glauber's salt with cold

<sup>1</sup> *Phil. Trans. Roy. Soc.*, 174, 910.

<sup>2</sup> *Chem. News*, 78, 229.

<sup>3</sup> *Ann. chim. phys.*, (7), 19, 192.

<sup>4</sup> *Compt. rend.*, 87, 632.

<sup>5</sup> *Compt. rend.*, 88, 322; 89, 212.

<sup>6</sup> *Arch. des Sci. phys. et nat.* (3), 3, 413.

<sup>7</sup> *Compt. rend.*, 102, 902.

<sup>8</sup> *Loc. cit.*, 93, 63.

water, his decipia of two years before could be decomposed into two oxides, one with a metal equivalent of about 130 (RO) giving no absorption spectrum, the other with a base of much lower equivalent (not over 117) giving the absorption spectrum ascribed to the original decipia. He expressed the opinion that this second oxide and samaria were identical, as well as Marignac's  $Y_{\beta}$ . He also thought that the earth  $Y_{\alpha}$  was a mixture of decipia and terbia, but Marignac pointed out that this could not be, because the oxide of  $Y_{\alpha}$  was white, whereas that of terbium was colored. The oxide of  $Y_{\alpha}$  and decipia were perhaps identical.

Cleve<sup>1</sup> has made an exhaustive study of samaria and its compounds. He isolated it by combining the methods of fractional precipitation with potassium sulphate solution, and with dilute ammonia. The atomic weight of samarium he found to be 150.02 ( $R^{III}$ ). Its spark spectrum has been described by Thalén<sup>2</sup> and by Lecoq de Boisbaudran<sup>3</sup>. The latter also studied its fluorescence spectrum. The body giving the spark spectrum he called  $Z_6$ , the one giving the fluorescence  $Z_7$ . Demarçay<sup>4</sup> found that samarium could be split into at least two simpler constituents. He used three methods, Welsbach's, fractional precipitation with ammonia, and another not given. He kept the name samarium for the element giving  $\lambda_{407}$  and  $\lambda_{400}$ , and called the other provisionally S. Krüss and Nilson,<sup>5</sup> in an article on the rare earths giving absorption spectra, also observed the fact that solutions containing samarium did not always give the same absorption spectrum. They obtained some solutions showing only  $\lambda_{417}$ , and the body to which this band was due they called  $Sm_{\alpha}$ . Crookes<sup>6</sup> in 1886, following the fractionation of samarium by examination of the phosphorescence spectra, concluded that the samarium of gadolinite enclosed three components, while the samarium from samarskite contained a fourth. He<sup>7</sup> also observed an anomalous ray in the phosphorescence spectrum of samarium. Its wavelength was 609, and the body to which it was due he called  $S_{\alpha}$ .

<sup>1</sup> *Compt. rend.*, 97, 94; *Bull. Soc. Chim.*, (2), 43, 162; *Chem. News*, 83.

<sup>2</sup> *Sv. Vet. Akad. Handl.*, No. 7, p. 3 (1883); *J. de Phys.*, (2), 2, 446; *Ber. d. chem. Ges.*, 16, 2760.

<sup>3</sup> *Compt. rend.*, 114, 575; 116, 611, 674; 117, 199.

<sup>4</sup> *Loc. cit.*, 102, 1551.

<sup>5</sup> *Ber. d. chem. Ges.*, 20, 2134.

<sup>6</sup> *Proc. Roy. Soc.*, 40, 502.

<sup>7</sup> *Compt. rend.*, 102, 1464.



In 1891 Bettendorff<sup>1</sup> obtained pure samaria by fractionation with ammonia, after the removal of ceria by fusion of the nitrates with potassium nitrate, the yttria group by treatment with potassium sulphate, and lanthana by decomposition of the nitrates by heat. He described the absorption spectrum, and denied that it had a phosphorescence one. He thought that samarium was a chemical individual. In 1893 Demarçay<sup>2</sup> decided that, as far as the absorption spectrum showed, there was no reason to suspect the complexity of samarium. He examined four different fractions of Lecoq de Boisbaudran's samarium material. In 1900 Demarçay<sup>3</sup> separated samaria from neodidymia by fractional crystallization of the magnesia double nitrates from nitric acid solution.

Crookes<sup>4</sup> questioned the individuality of gadolinium, stating that its phosphorescence spectrum was practically identical with that of a mixture of 61 parts of yttria and 39 of samaria. Lecoq de Boisbaudran<sup>5</sup> did not agree with him. Lecoq found, however, that Marignac's gadolinia contained about 10 per cent. of impurities, and he succeeded in removing all but about 0.02 or 0.03 per cent. of these. Crookes<sup>6</sup> described its phosphorescence spectrum, and Lecoq<sup>7</sup> its spark spectrum. Bettendorff<sup>8</sup> separated gadolinia from samaria and terbia by fractionation with ammonia. He could get no spark spectrum, nor could Thalén. In 1896 Demarçay<sup>9</sup> prepared gadolina by fractional crystallization of the earths rich in samaria from fuming nitric acid (sp. gr., 1.45), and gave the rays of its spark spectrum. Gadolinia was precipitated first, and samaria last. Between the two he discovered a new earth which he called  $\Sigma$ , characterized by its colorless salts with no absorption. The earth was colorless, which distinguished it from terbia; its spark spectrum was different from those of lanthana, ceria, gadolinia, ytterbia, terbia. It differed from gadolinia and samaria only in its spark spectrum. In 1899 Benedicks,<sup>10</sup> using Marignac's method partly, and partly by fusion of the ni-

<sup>1</sup> *Ann. Chem. (Liebig)*, 263, 164.

<sup>2</sup> *Compt. rend.*, 117, 163.

<sup>3</sup> *Loc. cit.*, 130, 1185.

<sup>4</sup> *Chem. News*, 84, 39, 115.

<sup>5</sup> *Compt. rend.*, 108, 165; 111, 393.

<sup>6</sup> *Ibid.*, 102, 646.

<sup>7</sup> *Loc. cit.*, 111, 472.

<sup>8</sup> *Ann. Chem. (Liebig)*, 270, 376.

<sup>9</sup> *Compt. rend.*, 122, 728.

<sup>10</sup> *Ztschr. anorg. Chem.*, 22, 393.

trates, then their fractionation from concentrated nitric acid, and lastly their precipitation by ammonia, prepared gadolinia and studied it. He could not obtain Demarçay's  $\Sigma$ . His gadolinia gave a spark spectrum, and the atomic weight of the metal was 156 ( $R^{III}$ ). Demarçay,<sup>1</sup> in 1900, was unable to isolate  $\Sigma$ , even after 800 fractions with the magnesia double nitrates; but since then he<sup>2</sup> has isolated it sufficiently pure for characterization. He has named it europium.

Marignac,<sup>3</sup> in trying to isolate Delafontaine's philippia by partial decomposition of the nitrates by heat, discovered a new earth which he called ytterbia. It was colorless, and its metal had a high atomic weight ( $R^{III} = 172.5$ ); further, it had no absorption spectrum. The method he used was a modification of Bahr and Bunsen's. He heated the nitrates till a portion was insoluble in hot water, whereas they heated only until the mass, which was entirely soluble in hot water, gave a crystalline precipitate of basic nitrates on cooling. In 1879 and 1880, Nilson<sup>4</sup>, using Marignac's method, isolated more ytterbia, and studied it. He found the atomic weight of the metal ytterbium to be 173. Pure ytterbia was obtained only after 400 or 500 ignitions. While working with this material, he obtained a white oxide whose metal equivalent was lower than that of ytterbia. This caused him to suspect the presence of another oxide, the metal of which had a lower atomic weight. By following the same method of fractionation, he<sup>5</sup> succeeded in isolating this earth. Its base had an atomic weight of 44, and proved to be identical with Mendeléeff's ekaboron, both in its properties and its atomic weight. He called his earth scandia. Cleve<sup>6</sup> also prepared scandia. His atomic weight of scandium was a unit higher than Nilson's, probably because of ytterbium in the material. The spark spectrum of ytterbia has been studied by Thalén<sup>7</sup> and by Lecoq de Boisbaudran<sup>8</sup>; that of scandia by Thalén.<sup>9</sup>

Solet,<sup>10</sup> by a spectroscopic examination of Marignac's erbia and

<sup>1</sup> *Compt. rend.*, 130, 1019.

<sup>2</sup> *Loc. cit.*, 132, 1484.

<sup>3</sup> *Arch. des Sci. Phys. et. nat.*, (2), 64, 97; *Compt. rend.*, 87, 578.

<sup>4</sup> *Ber. d. chem. Ges.*, 13, 550; 13, 1430.

<sup>5</sup> *Ber. d. chem. Ges.*, 12, 554; 13, 1439.

<sup>6</sup> *Bull. Soc. Chim.*, (2), 31, 486.

<sup>7</sup> *Chem. News*, 47, 217; *Compt. rend.*, 91, 326.

<sup>8</sup> *Compt. rend.*, 88, 1342.

<sup>9</sup> *Loc. cit.*, 88, 646; 91, 45; *Chem. News*, 47, 217.

<sup>10</sup> *Compt. rend.*, 86, 1062.

terbia materials, found a series of absorption bands which did not belong to erbia or to any other of the known elements. He called the earth giving them X. Cleve,<sup>1</sup> in 1897, showed that by fractional decomposition of the nitrates by heat, erbia free from ytterbia and scandia could be separated into three earths, each characterized by an absorption spectrum which was a portion of the one ascribed to old erbia. The metals in these earths were the true erbium, with an atomic weight of about 166;<sup>2</sup> holmium, and thulium with an atomic weight of about 170.7.<sup>3</sup> Soret<sup>4</sup> stated that holmia and his earth X were identical, and Cleve<sup>5</sup> admitted this to be true. Delafontaine maintained that his philippia was identical with both of these, but Cleve could not establish this fact. Delafontaine himself afterwards admitted that his philippia had no absorption spectrum. Lecoq de Boisbaudran<sup>6</sup> proved, by making many hundreds of fractions with ammonia and with potassium sulphate and alcohol, that the holmia spectrum could be divided into two portions, the bands characteristic of one being  $\lambda 640.4$  and  $\lambda 536.3$ , and of the other  $\lambda 451.5$  and  $\lambda 753$ . Since the first two bands were the ones by which Cleve and Soret originally characterized the element holmium, he kept this name for the one giving them; the one to which the other bands were due he called dysprosium. Crookes,<sup>7</sup> soon after Lecoq's announcement, stated that he had isolated an earth in this group giving only the absorption band  $\lambda 451$ , and that therefore dysprosium was probably still a complex substance. Lecoq has expressed the same opinion. Krüss and Nilson<sup>8</sup> showed, by a spectroscopic examination of the absorption bands of the rare earths obtained from many different minerals, that the variations in intensities of the bands as found in these minerals, could be accounted for only upon the assumption that the bands belonged to different individuals. As a result of this, they considered what we now call erbia to be made up of two components, thulia of two, holmia of four, and dysprosia of three. Hofmann and Krüss<sup>9</sup> in 1893 concluded, as a result of their aniline hydro-

<sup>1</sup> *Loc. cit.*, 89, 478.

<sup>2</sup> *Compt. rend.*, 91, 381.

<sup>3</sup> *Loc. cit.*, 91, 328.

<sup>4</sup> *Loc. cit.*, 89, 521.

<sup>5</sup> *Loc. cit.*, 89, 708.

<sup>6</sup> *Loc. cit.*, 102, 1003, 1005.

<sup>7</sup> *Proc. Roy. Soc.*, 40, 502.

<sup>8</sup> *Ber. d. chem. Ges.*, 20, 2134.

<sup>9</sup> *Ztschr. anorg. Chem.*, 3, 407.

chloride fractionation, that holmium was a complex substance; Krüss<sup>1</sup> alone has thrown doubt upon the individuality of erbia. By fractionation of his material rich in erbia from alcoholic solution with an alcoholic solution of aniline, then of the middle portions of this series as earth chloride aniline hydrochloride by ammonia, he could not get an earth whose base had a constant atomic weight. The beautiful absorption spectrum of erbia was discovered by Bahr<sup>2</sup> in 1862. Crookes<sup>3</sup> mapped all of the spectra of erbia. The absorption, emission, and spark spectra of thulia have been studied by Thalén.<sup>4</sup>

In 1883 Crookes<sup>5</sup> discovered that the anhydrous sulphates of certain rare earths became phosphorescent when exposed to the electric discharge in a vacuum tube, and that this light gave characteristic spectra. He<sup>6</sup> had in 1881 observed that some of the earths themselves phosphoresced under the same conditions. In 1883 he discovered in these phosphorescence spectra the citron band which he decided to be due to yttria. In 1884, Lecoq de Boisbaudran<sup>7</sup> discovered that if the positive pole were immersed in a solution of some of the rare earths, and the negative one brought just above its surface, the light which was emitted on the passage of the spark gave an inversion spectrum which was nearly related to the phosphorescence spectrum of Crookes. Both were very delicate, and were greatly influenced by the presence of foreign oxides.

In 1886 and the year following Crookes<sup>8</sup> separated yttria by a large number of different fractionations into five portions, each of which had different phosphorescence spectra, but all of which showed the spark spectrum of yttria. The bodies responsible for these phosphorescence spectra he called "meta-elements," and he developed his theory of the genesis of the elements on the basis of this observation. In further support of the idea that yttria was a complex substance, he stated that Marignac's gadolinia gave him the same phosphorescence spectrum as yttria, except that the citron band was missing, and that the two green bands of samaria were present. Then a mixture of 61 parts of yttria

<sup>1</sup> *Loc. cit.*, 3, 353.

<sup>2</sup> *Sv. Vet. Akad. Handl.*, p. 597 (1862); *Ann. Chem. (Liebig)*, 131, 256.

<sup>3</sup> *Chem. News.*, 83, 75.

<sup>4</sup> *Chem. News.*, 47, 217; *Compt. rend.*, 91, 376.

<sup>5</sup> *Phil. Trans. Roy. Soc.*, 174, 891; *Chem. News*, 47, 261; 49, 159, 169, 181, 194, 205.

<sup>6</sup> *Chem. News*, 44, 23; *Proc. Roy. Soc.*, 32, 209.

<sup>7</sup> *Compt. rend.*, 100, 1437.

<sup>8</sup> *J. Chem. Soc.*, 88, 250; *Chem. News*, 84, 115; 88, 83, 95.

with 39 of samaria gave the same phosphorescence as gadolinia, except for the presence of the citron band. He also found that the yttria from different minerals gave phosphorescence spectra with its rays of varying intensity, showing that a partial separation had taken place in nature.

This theory and all its conclusions were opposed by Lecoq de Boisbaudran.<sup>1</sup> He<sup>2</sup> showed that pure yttria gave no phosphorescence phenomena, either by his method or by that of Crookes. According to him, the fluorescence bands were attributable to impurities, to his substances  $Z_a$  and  $Z_\beta$ , in fact, and these it was almost impossible to remove completely from the yttria.<sup>3</sup> In connection with these substances giving fluorescence bands, he<sup>4</sup> has studied a considerable number of fluorescences with well-defined spectral rays, having for solid solvents alumina, gallium oxide, silica, zirconia, stannic and tantalic oxides, and for active matter samaria and the oxides of  $Z_a$  and  $Z_\beta$ . Demarçay<sup>5</sup> opposed Crookes' theory of "meta-elements," and stated that the radiant matter test of Crookes was far more delicate than the reversion spectra of Lecoq de Boisbaudran.

Duboin<sup>6</sup> made some compounds of yttria in the dry way. The accepted atomic weight of yttrium, 89.02 with O = 16 as the standard, is the one obtained by Cleve<sup>7</sup> in 1882. Rowland<sup>8</sup> published a method for the separation of yttria from other earths of its group by means of potassium ferrocyanide. His paper was severely criticized by Crookes.<sup>9</sup>

In 1896 Barrière<sup>10</sup> announced the existence, in the yttria earths from monazite, of a new metal which was separated from the other members of the group by precipitation with sodium thiosulphate in concentrated solution. This element, lucium, had an atomic weight of 104. Crookes,<sup>11</sup> by examination of its spark and absorption spectra, found that it was a mixture of yttrium and didymium, erbium and terbium, but was principally yttrium. Shapleigh<sup>12</sup>

<sup>1</sup> *Bull. Soc. Chim.*, (3), 3, 53.

<sup>2</sup> *Compt. rend.*, 102, 1536.

<sup>3</sup> *Compt. rend.*, 103, 113.

<sup>4</sup> *Loc. cit.*, 108, 258, 351, 343, 784; 110, 24, 67.

<sup>5</sup> *Rev. gen. des Sci. pures et appliquées*, 1, 396; *Chem. News*, 62, 85.

<sup>6</sup> *Compt. rend.*, 107, 99.

<sup>7</sup> *Loc. cit.*, 98, 1225.

<sup>8</sup> *Chem. News*, 70, 68.

<sup>9</sup> *Loc. cit.*, 70, 81.

<sup>10</sup> *Chem. News*, 74, 159, 212.

*Loc. cit.*, 74, 259.

<sup>12</sup> *J. Franklin Inst.*, 144, 68; *Chem. News*, 76, 41.

found by a quantitative analysis of a sample of lucia that it contained 93.98 per cent. of yttria earths, 3.74 per cent. of ceria earths, 1.07 per cent. of thoria, and 1.21 per cent. of other foreign oxides.

In 1896 and 1897 Schützenberger and Boudouard<sup>1</sup> worked on the yttric earths of monazite sands. They found by fractional fusion of the nitrates and by fractional crystallization of the sulphates that a lower limit of fractionation was reached, giving an earth whose metal-equivalent ( $R_2O_3$ ) was about 95. They thought that they had found a new earth, whose metal had an atomic weight of about 102. Drossbach,<sup>2</sup> working also on monazite, thought he had a new earth similar to the others (the atomic weight of its base, 100). Further, Urbain and Budischovsky,<sup>3</sup> fractioning the yttria earths by means of the acetyl acetates, found a similar lower limit. Urbain,<sup>4</sup> working with the ethyl sulphates, succeeded in showing that this hypothetical earth could be separated into terbia ( $R^{III} = 151.4$ ) at one end of his fractionation series, and yttria ( $R^{III} = 89$ ) at the other. In 1900 Urbain<sup>5</sup> again took up the question of this earth, and concluded that it was principally yttria, mixed with some erbia and terbia. This lower limit of various fractionation series, giving a base of nearly constant atomic weight, reminds one of the "oxide of gadolinium" of Nordenskjöld.<sup>6</sup> This was a rare earth mixture, obtained from different minerals, which he knew to contain at least three oxides, those of yttrium, erbium, and terbium, and yet its metal had a constant atomic weight of 107.

Crookes<sup>7</sup> in 1898 announced the existence of an element giving a group of phosphorescence bands in the ultraviolet only. He then called it monium. Its principal rays were  $\lambda_{3120}$  and  $\lambda_{3117}$ , and its atomic weight about 118. In 1899, he<sup>8</sup> renamed it victorium, and told how it was isolated. The method was a long combination of the standard ones of fusion of the yttria group nitrates, fractional precipitation of the oxalates from concentrated nitric acid solution, fusion of the nitrates again, and finally fractional precipitation with potassium sulphate.

<sup>1</sup> *Compt. rend.*, 122, 697; 123, 782; 126, 1648.

<sup>2</sup> *Ber. d. chem. Ges.*, 29, 2452.

<sup>3</sup> *Compt. rend.*, 124, 618.

<sup>4</sup> *Compt. rend.*, 126, 835; 127, 107.

<sup>5</sup> *Ann. chim. phys.*, (7), 19, 184.

<sup>6</sup> *Compt. rend.*, 103, 795.

<sup>7</sup> *Chem. News*, 78, 134.

<sup>8</sup> *Proc. Roy. Soc.*, 68, 237; *Chem. Centrbl.*, (1899) II, p. 748.

In addition to all of these earths, and, of course, ceria, lanthana, didymia and thoria, a few others have been announced. Their existence was generally short. Junonium was prepared in 1811 by Thomson<sup>1</sup> from allanite. Donarium was announced by Bergemann<sup>2</sup> in 1851. He prepared it by precipitating the silica-free acid solution of the mineral thorite with ammonia. Damour,<sup>3</sup> Berlin,<sup>4</sup> and finally Bergemann himself<sup>5</sup> thought that donaria was identical with thoria. Bahr<sup>6</sup> announced the discovery of wasium, which Nicklés<sup>7</sup> thought was a mixture of yttrium with didymium or terbium. Delafontaine<sup>8</sup> thought wasium was cerium, perhaps with some didymium. Popp<sup>9</sup> agreed with Delafontaine. Bahr<sup>10</sup> considered it probable that wasium and thorium were identical, and that both Nicklés and Delafontaine were mistaken in the matter.

Smith<sup>11</sup> announced the existence of two new elements in samarskite, which he called columbium and rogerium. This columbium is not, of course, to be confused with the well-known one. Chroustchoff<sup>12</sup> detected spectroscopically the existence of a new element, russium, in certain wash residues from rocks, in many alumina preparations, and in American monazite. He<sup>13</sup> prepared russium in much the same manner that Barrière prepared lucium. Linnemann<sup>14</sup> discovered austrium in the rare earth mixtures from orthite. Lecoq de Boisbaudran<sup>15</sup> considered it to be gallium. Pribram<sup>16</sup> decided that Linnemann's product was gallium, at the same time maintaining the probability of a new element in orthite.

#### EXPERIMENTAL.

In 1877 J. W. Mallett published an article on sipylite, a new niobate, from Amherst County, Virginia.<sup>17</sup> An analysis of the

<sup>1</sup> Gilbert's *Ann.*, 42, 115; 44, 113.

<sup>2</sup> *J. prakt. Chem.*, 53, 239.

<sup>3</sup> *Pogg. Ann.*, 85, 555.

<sup>4</sup> *Loc. cit.*, p. 556 and 87, 608.

<sup>5</sup> *Loc. cit.*, 85, 558.

<sup>6</sup> *Pogg. Ann.*, 119, 572; *J. prakt. Chem.*, 91, 179.

<sup>7</sup> *Compt. rend.*, 87, 740.

<sup>8</sup> *Ann. Chem.* (Liebig), 131, 368.

<sup>9</sup> *Loc. cit.*, 131, 364.

<sup>10</sup> *Loc. cit.*, 132, 227.

<sup>11</sup> *Nature*, 21, 146; *Chem. News*, 49, 182.

<sup>12</sup> *Berg. u. huet. Ztg.*, 46, 329; *Chem. Centrbl.*, p. 1277 (1887).

<sup>13</sup> *J. russ. phys. chem. Ges.*, 29, 206; *Chem. Centrbl.*, 11, 329 (1897).

<sup>14</sup> *Monatsh. Chem.*, 7, 121.

<sup>15</sup> *Compt. rend.*, 102, 1436.

<sup>16</sup> *Sitzungsber. d. k. Akad. d. Wiss., Wien, Div. 2b*, 109, 16; *Monatsh. Chem.*, 21, 148.

<sup>17</sup> *Am. J. Sci.*, 14, 397 (1877).

mineral made under his direction by W. G. Brown indicated the substance to be essentially a niobate of erbium containing some tantalic acid, about 1 per cent. of yttrium oxide and approximately 11.5 per cent. of the earths of the cerium group.

In the following year Delafontaine<sup>1</sup> examined this mineral and stated that it contained erbium, philippium, and ytterbium, the last-named element having been isolated but a short time before by Marignac.

A supply of sipylite which had been procured by one of us from Virginia and Texas was used as the source of the earths in this investigation. The mineral was finely powdered and was then mixed with a large excess of primary potassium sulphate, and this mixture was fused in deep iron dishes in a crucible furnace. When decomposition was complete, the mass was cooled, powdered, and thrown into ice-water, the water being stirred until complete solution of all soluble compounds had been effected. The clear supernatant liquid was then siphoned off, nearly neutralized with ammonia, and precipitated with oxalic acid. The oxalates were then washed, dried, ignited, dissolved in sulphuric acid, and precipitated with ammonium hydroxide. This precipitate, after thorough washing by decantation, was dissolved in nitric acid and to the neutral solution there was then added a saturated solution of potassium sulphate and crystals of the same salt. The mixture was violently stirred until the supernatant liquid failed to show the absorption bands of didymium. The resulting precipitate of the earths of the cerium group was removed by filtration, and was washed with a saturated solution of potassium sulphate. The filtrate was diluted with water and was precipitated by a solution of oxalic acid. These mixed oxalates which, of course, still contained traces of the earths of the cerium group, were dried and ignited. The resulting mixture of oxides weighed about 350 grams and was of a deep orange-yellow color.

The atomic weight of the oxide mixture, assuming that all the oxides present were of the  $R_2O_3$  type, was determined by the oxalate method of Gibbs and the sulphate method of Krüss, and was found to be in the neighborhood of  $R^{III} = 108$ . Assuming that the average atomic weight of the elements other than yttrium lies in the neighborhood of 165, this result shows that the mixture consists largely of yttrium oxide, approximately 75 per cent.

<sup>1</sup> *Compt. rend.*, 87, 933.



The absorption spectrum when observed through a 10 cm. layer of the saturated solution of the nitrate of the mixture showed the bands tabulated below. The measurements in the table coincide with the maximum intensities of the absorption bands unless otherwise indicated.

Angle.	Wave-length $\lambda$ .	Element.	Description of band.
12° 2' 30"	6832.4	{ Erbium Thulium	Faint, rather broad, edges vague.
11° 45' 10"	6670.7		Slightly stronger than 6832.4
11° 29' 00"	6519.9	{ Erbium	Moderately broad and strong with two maxima, one in center, the other at right edge.
11° 25' 20"	6485.7		
11° 16' 40"	6404.7	Holmium	Moderately strong, right edge sharp, maximum to right of center.
10° 11' 50"	5797.9	{ Didymium	Edges of broad, very hazy band. Scarcely visible.
10° 4' 00"	5725.5		
9° 39' 50"	5497.7	Unknown (Crookes)	Faint.
9° 30' 30"	5410.0	Erbium	Broad strong band, two maxima, one to left of center, the other at right edge.
9° 25' 30"	5363.0	Holmium	
9° 11' 10"	5228.2	{ Erbium	Strongest band in spectrum, two maxima, one at left edge, the other in center. Right edge indistinct.
9° 6' 40"	5185.9		
8° 32' 20"	4862.7	Samarium	Almost as strong as 5228.2. Extends from $\lambda$ 4938.1 to $\lambda$ 4825. Maximum to left of center.
8° 17' 10"	4719.8	Samarium	Very faint.
8° 11' 50"	4669.5	Samarium	Very faint.
7° 54' 00"	4501.3	Dysprosium	Almost as strong as 5228.2. Extends from $\lambda$ 4550.0 to $\lambda$ 4449.4.
7° 43' 40"	4403.8	Didymium (?)	Very faint.
7° 16' 50"	4150.3	Samarium	Faint and hazy.

The measurement of the positions of the absorption bands was made with a small grating spectroscope manufactured for one of us by C. A. Steinheil Sons, of Munich. This instrument is so compact and convenient and the accuracy of the readings which can be made with it so far surpasses that attainable with a prism

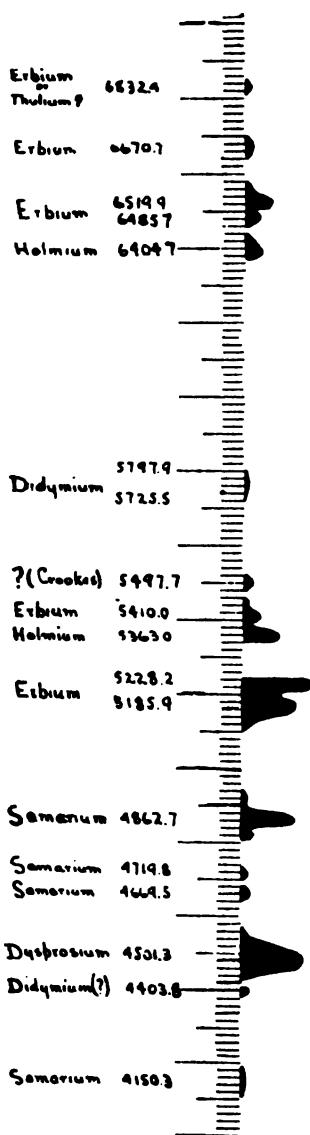


FIG. 1.

turned to bring the line into the position occupied by the image of the slit at the zero point. It is obtained by the formula  $\lambda = \frac{K \sin \omega}{n}$ ,  $K$  being the constant of the instrument, and  $n$  the order

spectroscope as perhaps to justify the insertion here of a brief description of the instrument. The box of the apparatus carries the plate *EFGH* (Fig. 2) as a cover, and upon this a divided quadrant *LMN*, a vernier and a microscope. Inside the box are the grating *D*, the prism *P* and the mirror *K*. The grating is turned about the axis *a* by the vernier-arm *Q*. *A* is the collimator tube with slit *J*, *B* the telescope, and *C* the scale tube. The parallel rays from the collimator-objective are reflected by the prism in the direction *Pa* upon the grating *D* and from there are reflected in the direction *aO*. When the grating is so placed that the perpendicular to its plane bisects the angle *PaO*, one sees through the telescope the image of the slit reflected from the grating. The zero point of the instrument is obtained by placing the cross hairs of the eye-piece over the image of the slit. Both the quadrant and the vernier are so divided that the grating may be turned either way, the readings for the same line on either side of the zero being thus the same. The quadrant is divided into intervals of 10'; the vernier may be read to 10". The scale tube *C* may be turned on an arm so that it may be used for spectra of the second and third orders. The wave-length of the line measured is a function of the angle through which the grating must be

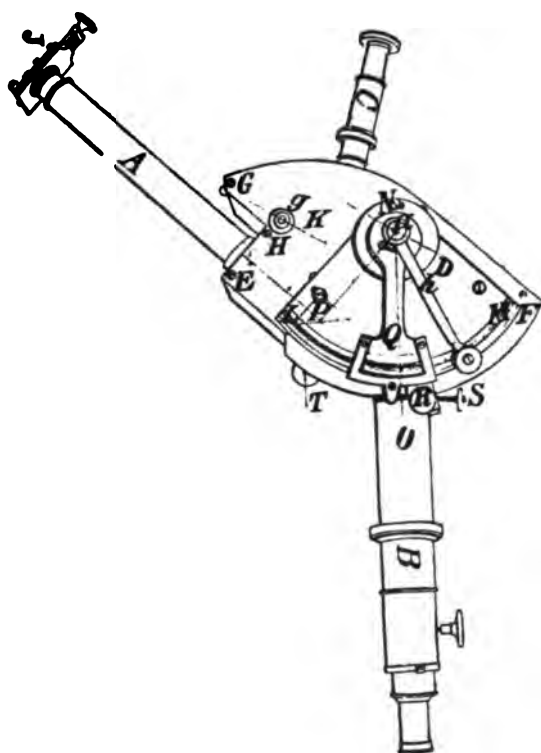


FIG. 2.

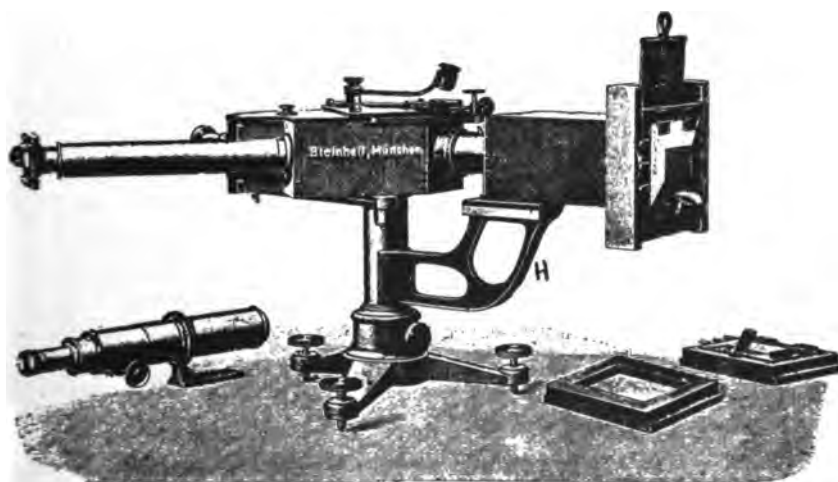


Fig. 3.

of the spectrum. Fig. 3 shows the instrument with a camera attachment substituted for the telescope tube. As the source of light a zirconia disk and a Linnemann oxyhydrogen blowpipe were used.

#### THE DETERMINATION OF THE ATOMIC WEIGHTS OF THE ELEMENTS.

The method described by Gibbs<sup>1</sup> was used when only an approximate result was desired. The procedure was as follows: A neutral or only very slightly acid solution of the earths whose atomic weight is to be determined is diluted with water, brought nearly to the boiling-point, and is then precipitated with a hot dilute solution of pure oxalic acid. The precipitate is washed by decantation and on the filter with hot water to remove the excess of oxalic acid and is then dried at a temperature of 125°. A weighed portion of the oxalate precipitate is then converted to the oxide by ignition and this oxide is weighed. Another weighed portion of the oxalate is dissolved in dilute sulphuric acid (1:8) and the oxalic acid is determined by titration with potassium permanganate. The atomic weight of the earths in the mixture of the rare earths is then easily calculated from the ratio of  $R_2O_3$ :  $C_2O_3$ . This method of determining the atomic weights gives results that are sufficiently accurate to enable one to judge of the progress of a method of separation or fractionation, but which are far from being exact, and comparison of the method with the sulphate method showed that the Gibbs procedure gave results differing by as much as four units from the sulphate method of Krüss. To ascertain the effect of changes in the conditions prevailing at the time of precipitation the following experiments were made.

A solution of the earths was carefully freed from other elements by precipitating it with hydrogen sulphide, filtering off a very slight precipitate which formed, boiling the filtrate to remove the hydrogen sulphide and precipitating it with ammonia, dissolving the washed precipitate in hydrochloric acid, and after nearly neutralizing with ammonia, precipitating this solution with oxalic acid. The oxalates thus obtained were washed with very dilute hydrochloric acid (0.1 per cent.) to remove iron, then with water, and were then dried, ignited, and the resulting oxides were dissolved in hydrochloric acid. This chloride solution was divided

<sup>1</sup> *Am. Chem. J.*, 18, 547.

into two parts. One was precipitated with a hot and dilute solution of oxalic acid, while the other was precipitated in the cold and in more concentrated condition with a cold concentrated solution of oxalic acid. Another portion of the same original material was purified and treated in exactly the manner described above, and was divided and precipitated in the same way. The results of the atomic weight determinations of these various portions by the oxalate method were as follows :

	Hot.	Cold.
1	111.28	108.26
2	105.06	104.70

The variations in these results show that they are greatly influenced by changes in the conditions, and that they by no means agree even when the same conditions pertain.

The other method employed for the determination of the atomic weights was that described by Krüss.<sup>1</sup> In this procedure the oxalate of the earth is placed in a porcelain crucible and ignited over a blast-lamp to constant weight. The crucible containing the oxide is placed on a water-bath, covered with a funnel, and the heating of the water-bath is continued until the water vapor has slowly and completely slaked the oxide. The substance is then dissolved in the crucible with dilute hydrochloric acid. A moderate excess of dilute sulphuric acid is added and the solution is concentrated as far as possible on the water-bath. The excess of sulphuric acid is removed by placing the crucible on an iron plate 5 mm. thick and heating the plate with a small Bunsen flame. This is continued until constant weight is obtained, and from the ratio of the oxide to the anhydrous sulphate, the atomic mass of the earth or earths present is calculated. Considerable difficulty was experienced in making duplicate analyses agree satisfactorily. The probable explanation of this trouble is to be found in the article by Brauner and Pavlicek,<sup>2</sup> in which those authors call attention to the fact that the sulphate which is finally weighed is liable to contain some acid sulphate. This acid sulphate is so stable that some of it remains undecomposed even at a temperature above 500°, while in other parts of the crucible it may have partially been broken down into a basic sulphate. They state that the error is greatest in the case of lanthanum and that it decreases as the basicity of the earth decreases. They deter-

<sup>1</sup> *Ztschr. anorg. Chem.*, 2, 46.

<sup>2</sup> *Proc. Chem. Soc.*, London, 17, No. 235, p. 63.

mine the amount of sulphuric acid which is present in excess over the amount necessary to form the normal sulphate by dissolving the dry sulphates in water and titrating the free sulphuric acid with a twentieth normal solution of sodium hydroxide using ethyl orange as an indicator. The normal sulphate obtained by repeated crystallization was found by them to be neutral to ethyl orange.

These statements concerning the sulphates of the earths of the cerium group hold true for those of the yttrium group, but the error is less because the basicity of the earths of this group is less. For example, two weighed portions of a sulphate which had given  $R^{III} = 115.90$  and  $116.42$ , were dissolved in water and the excess of free acid titrated as above, using methyl orange as an indicator. The corrected results for these two samples were  $R^{III} = 116.19$  and  $116.47$ . Another set which had given  $R^{III} = 141.22$  and  $141.53$  gave after correction  $141.51$  and  $141.73$ . A third set giving  $R^{III} = 107.31$  and  $106.75$  gave after correction  $107.37$  and  $106.92$ . There seems to be no regularity in the amounts of acid sulphate which are formed. The maximum error caused by its presence seems to be about 0.3 of a unit. All of the solutions which were tested showed an acid reaction, but in some cases a drop or two of the solution of sodium hydroxide was sufficient to neutralize the free acid. The results of duplicate determinations were usually brought to closer agreement by the introduction of the correction. In only one case was the opposite effect noted.

#### EXPERIMENTS UPON METHODS FOR SEPARATING YTTRIUM GROUP EARTHS.

The aim which the authors had in view in this work was not so much the isolation of one or another constituent of the mixture of the rare earths, but rather the study of various methods of separation to ascertain along what lines different treatments will cause the earths to separate. A complete systematic study of the different methods of separation was also not undertaken, for those procedures which give slow results and in which the successive treatments are of but slight effect upon the rare earth mixture, can not be successfully employed, because of the time which is consumed and of the incompleteness of the separation which they bring about. Therefore, in the trials of the different

methods to be described below it will be seen that the procedure was abandoned as soon as it became apparent that only slow separation was being effected.

#### FUSION OF THE YTTRIUM GROUP NITRATES WITH ALKALI NITRATES.

The method first tried was that of fusion of the rare earth nitrates with alkali nitrates, proposed by Debray, and which, as modified by Dennis and Magee,<sup>1</sup> gives such satisfactory results in separating cerium from the other members of the group. It was hoped that the decomposition points of some of the yttria group double nitrates might be found sufficiently far apart to admit of a sharp separation, but such was not the case.

The dry yttrium group nitrates were mixed with six times their weight of a molecular mixture of potassium and sodium nitrates, placed in a deep porcelain evaporator, and fused in a large double air-bath, the space between the walls of the bath being filled with infusorial earth to prevent radiation. Three fusions were made and after each the substance was extracted with hot water, yielding an insoluble and a soluble portion. Fusions were made at three temperatures, 280°, 320°, and 360°, using different mixtures each time. These temperatures were measured by means of a Le Chatelier pyrometer manufactured by Keiser and Schmidt, of Berlin. Each portion was fused for about three hours. The results were irregular and gave no indication of a sharp separation by this method, as the following atomic weights show.

Atomic weight of the initial metal mixture, 108.19.		
Insoluble.	Temperature.	Soluble.
114.70	280°	108.31
127.55	320°	108.14
112.24	360°	102.43

A comparison of the absorption spectra of solutions of these portions and of the original material with a direct-vision spectro-scope showed no appreciable differences.

#### PARTIAL PRECIPITATION WITH HYDROCHLORIC ACID GAS.

Partial precipitation of the anhydrous chlorides by hydrochloric acid gas from a cooled solution was next tried. A concentrated solution of the chlorides ( $R^{III} = 107.94$ ) was placed in a gas wash-bottle surrounded by a freezing-mixture of ice and salt; hydro-

<sup>1</sup> This Journal, 16, 653.

chloric acid gas from a Norblad generator was then passed through the liquid for about five hours. Quite a heavy white crystalline precipitate was obtained. This was thrown on to a porous plate and drained. It is very deliquescent. The concentrated solution of the crystals had a yellow color. The mother-liquor changed color from rose to orange while saturated with hydrochloric acid, due probably to the forcing back of the dissociation of the chloride by hydrochloric acid.

The mother-liquor was precipitated with ammonia and washed to remove chlorides, the precipitate dissolved in hydrochloric acid, concentrated and again treated for two hours with hydrochloric acid gas in the freezing-mixture. Another heavy white crystalline precipitate was obtained, which gave a slightly yellow solution.

The spectra of the original solution and of saturated solutions of these two precipitates were compared by means of the small comparison spectroscope manufactured by Zeiss of Jena and described by Dr. Pulfrich in the *Zeitschrift für Instrumentenkunde*, October, 1900. No changes in the relative intensities of the various bands were visible.

#### PARTIAL DECOMPOSITION OF THE CHROMATES.

Pattison and Clarke<sup>1</sup> separated cerium from lanthanum and didymium by heating the normal chromates to 230° F. for some hours. The method when tried on this material gave no separation whatever. About 3 grams of the oxides ( $R^{III} = 103.75$ ) were dissolved in concentrated chromic acid and the solution evaporated to dryness. The dry mass was heated for six hours at a temperature of about 200° but decomposition merely on the surface was the only result, as could be told by the change in color from the red of the chromate to the green of the chromic oxide. This same substance was then pulverized and heated for six hours to 250° with practically the same result. The substance was extracted with hot water, yielding a red solution and a greenish black residue. The solution was evaporated to dryness and was then heated to 300° for eight hours, but only very slight decomposition resulted. The insoluble greenish black residue was again obtained from this portion. These two residues were treated with hot hydrochloric acid, and the green solution which was obtained was neutralized with ammonia and precipitated with

<sup>1</sup> *Chem. News*, 16, 259.



oxalic acid. Only a faint trace of the rare earth oxalates were thrown down.

#### FRACTIONAL PRECIPITATION WITH POTASSIUM CHROMATE.

The first to use this method in the separation of the rare earths was Gerhard Krüss.<sup>1</sup> This has since been modified by Moissan<sup>2</sup> and in this form was employed by the authors on the material which gave  $R^{III} = 107.94$ . Krüss added a neutral solution of potassium chromate to a neutral nitrate solution of the earths, while Moissan used a sulphate solution of the earths, neutralizing the liquid with ammonium hydroxide before each fractional precipitation with potassium chromate. The authors followed Moissan's directions carefully, but used a solution of the nitrates of the rare earths instead of the sulphates. This nitrate solution, amounting to 15 liters and containing about 140 grams of the oxides was first neutralized with ammonium hydroxide and 1 liter of the solution of potassium chromate containing 97 grams to the liter was added with continual stirring. The precipitation was carried on in tall glass cylinders of about 10 liters' capacity. The flocculent precipitate was allowed to settle and the red supernatant liquid was removed by means of a siphon. The precipitate was washed with water until the wash-water gave no precipitate with ammonium hydroxide. The earths in the wash-water were recovered by precipitation with ammonium hydroxide and this precipitate was dissolved in nitric acid to a neutral solution and was added to the mother-liquor. This liquid was then again carefully neutralized with ammonium hydroxide and was then treated with the same amount of potassium chromate solution as was used for the first fraction. This procedure was repeated four times, giving in all five fractions. The mother-liquor and wash-water from the last fraction were precipitated by ammonium hydroxide yielding fraction 6. With each succeeding precipitation the dilution of the solution was increased by about 1 liter.

Precipitate 1 was so small in amount as to render its separate treatment inadvisable; it was therefore united to precipitate 2 and the two were treated as one fraction. Each precipitate was dissolved in dilute hydrochloric acid, the chromic acid was reduced by adding alcohol and heating on the water-bath, and the resulting green solution was then nearly neutralized with ammonia,

<sup>1</sup> *Ztschr. anorg. Chem.*, 3, 92.

<sup>2</sup> *Compt. rend.*, 122, 573.

heated to boiling, and precipitated with a boiling solution of oxalic acid. In each case the precipitated oxalates were washed with a 1 per cent. solution of hydrochloric acid and were then dried and ignited. The resulting oxide was dissolved in hydrochloric acid. For the atomic weight determinations by the Gibbs method a portion of each of these solutions was precipitated with oxalic acid and the oxalate was washed and dried.

Fraction 1 gave a pink oxalate, a deep orange oxide, and its saturated solution of a brownish-yellow color showed the same absorption bands as the original solution, but the bands were slightly stronger.

Fraction 2 was practically identical with fraction 1.

Fraction 3 gave a pink oxalate and an orange-yellow oxide somewhat lighter in tint than the oxide from fraction 2. Its saturated solution showed all of the absorption bands strongly.

Fraction 4 yielded an oxide somewhat lighter in color than that from fraction 3, and its solution showed the bands plainly but not as plainly as the preceding fractions.

Fraction 5 gave an oxalate of a pale pink color and a very light yellow oxide. The saturated solution of its oxide was much paler in color than the solutions of the preceding fractions, and while it showed all of the absorption bands they were much less distinct than in fraction 4.

Fraction 6 gave a perfectly white oxalate and the oxide showed only the faintest tinge of buff color, and its solution had a pale greenish-yellow tint. The absorption bands of this last solution were quite weak.

The atomic weights of the original material and the six fractions with fractions 1 and 2 united are as follows :

Original, 107.94.				
1 and 2	3	4	5	6
133.54	126.13	114.04	97.83	94.01

Fractions 1, 2, 3, and 4 were then united and were again fractionally precipitated by the chromate method. The atomic weights of the three fractions thus obtained were 145.34, 127.38 and 103.75. The middle fraction was then split up into two parts, one showing an atomic weight of 150.03 and the other 124.53.

Fractions 5 and 6 contain yttria with about 10 per cent. of oxides having high atomic weights as terbia, erbia, and ytterbia.

These two fractions comprised nearly half the material used in the fractionation. After 7 grams of oxides with metal atomic weight of 107.07 had been extracted from them by this same process, the rest was set aside as yttria material. The two highest fractions  $R^{III} = 145.34$  and 150.03 were also set aside for future use.

It is thus seen that fractionation with potassium chromate separates the earths of this group with considerable rapidity. It is especially serviceable as a means of obtaining yttria free from the other earths, this substance being separated in quite pure form at the end of a comparatively short series of fractions. The mixture of oxides in the first fractions is still a very complicated one and further application of the chromate method does not appear to affect it appreciably.

#### FRACTIONAL PRECIPITATION WITH PRIMARY POTASSIUM OXALATE.

The separation of the earths with this method proceeds but slowly as is shown by the atomic weights given below. The method is a modification of the one used by Delafontaine for the separation of terbia from yttria and erbia. He added the solution of primary potassium oxalate to a solution of the rare earths until a point was reached at which another drop of the reagent caused a permanent precipitate. The liquid was then allowed to stand until the oxalates crystallized out. The solid substance was then removed and crystallization was repeated after the addition of more of the oxalate.

The authors used very dilute solutions in carrying on this method of fractionation, that of the primary potassium oxalate being about one-twelfth molecular, while the solution of the rare earths was diluted until the absorption bands were just visible with distinctness. The solution of primary potassium oxalate was made by dissolving in water molecular proportions of potassium oxalate and oxalic acid.

In order to be able to judge of the effect of fractional precipitation by this method upon the absorption bands of the solution, the precipitation was carried on before the spectroscope. The solution of the rare earths was transferred to a large crystallizing dish about 20 cm. in diameter and this dish was placed directly before the slit of a Steinheil grating spectroscope. Light was furnished by a Linnemann zircon-disk lamp. The solution was

kept in constant motion by means of a stirrer run by a Porter electric motor, and the solution of the primary potassium oxalate was added drop by drop from a burette. Before beginning the fractionation it is necessary to add a concentrated solution of the oxalate until a permanent precipitate just forms.

The first effect of the precipitation was to weaken the holmium bands, while all the bands decreased in intensity, the most persistent being the erbium band in the green. About 5 grams of the oxides were obtained from fraction 1. Half of the mother-liquor from this fraction was then precipitated and 6 grams were obtained. This halving of the solution was made necessary because of the limited size of the dish, and concentration was undesirable because of the possible disturbing action of the more concentrated oxalate solution upon the earths. The mother-liquor from fraction 2 was again divided and about 5 grams of oxides were obtained in fraction 3. At the end of this third fraction all of the absorption bands had disappeared with the exception of the erbium band in the green which was just visible. The mother-liquor from the last fraction amounting to one-fourth of the original solution was completely precipitated by the addition of the concentrated solution of primary potassium oxalate. Each of the precipitates was washed, dried, ignited, and dissolved in nitric acid. The oxalates of the first three fractions were pink while that of the last one was white. The oxides of the first three fractions were orange-yellow in color while that of the last fraction had a pinkish tinge. All the solutions showed the rose pink color of erbium salts. In determining the atomic weights, a portion of each nitric acid solution was precipitated with ammonium hydroxide and this precipitate was thoroughly washed with water to remove potassium salts. It was then dissolved in nitric acid to a barely acid solution and precipitated with oxalic acid.

Original, 112.16			
1	2	3	4
118.80	116.71	111.08	102.53

The precipitates which are thrown down by these oxalate reagents are finely crystalline and are consequently easily freed from the mother-liquor. Fractionation could probably be carried on with a fair degree of rapidity and interesting results might be obtained. The separation was, however, too slow for the authors' purposes and therefore no further trials have yet been made of it.

## FRACTIONAL DECOMPOSITION OF A SOLUTION OF THE MIXED NITRATES BY MEANS OF AN ELECTRIC CURRENT.

About 120 cc. of a solution of the nitrates ( $R^{III} = 107.94$ ) were carefully neutralized with ammonium hydroxide. This solution was placed in a Classen platinum electrolysis dish and was connected with the negative terminals of two cells of a storage battery. A platinum disk about 3 cm. in diameter was used as the positive electrode. A low current of  $N. D._{100} = 0.17$  to  $0.42$  ampere at a potential difference between electrodes of 2.2 to 2.7 volts was passed into the solution for about twenty hours, the solution being kept neutral and at room temperature (about  $21^{\circ} C.$ ). A white precipitate of the hydroxides was obtained at the cathode. A brownish deposit collected on the anode, but this was found to be lead dioxide due to a trace of lead present in the solution. The solution was poured off from the precipitate, the latter adhering to the dish sufficiently to make it possible to wash it without loss. The solution was evaporated to its original volume and was again submitted to electrolysis, with a current of  $N. D._{100} = 0.18$  to  $0.20$  ampere at 1.8 to 1.9 volts for seven hours at  $21^{\circ} C.$  Again there was a small amount of precipitate formed. This being non-adherent, it was removed by filtration and the wash-water and solution were again evaporated to the original volume and electrolyzed. A current of  $N. D._{100} = 0.17$  ampere failed to produce any further precipitation after six hours, so the current was raised to  $N. D._{100} = 0.33$  to  $0.42$  ampere with a potential difference of 2.45 to 2.55 volts and allowed to run for twenty-three hours. A further white precipitate was obtained. These two precipitates were united for the second fraction; the atomic weight of the fraction was then determined as was that of the first fraction and that of the residual solution. These three values compared with the original are as follows:

Original, 107.94.		
1	2	Residual solution.
120.22	116.61	106.20

If the decomposition voltages of the rare earths of this group were far enough apart to permit of a separation by means of electrolysis, the two fractions here should have atomic weights which differ more than do these. For if the earth or earth mixture which is thrown out of solution by a current of  $N. D._{100} = 0.17$  ampere at a potential difference between electrodes of about 2.5

volts was different from that which is precipitated by a current of about twice the density, the difference should show itself in the atomic weights. It is evident therefore that, under the conditions here prevailing, the separation of the rare earths can only slowly be effected.

#### FRACTIONAL PRECIPITATION WITH MAGNESIA USTA.

Muthmann and Rölzig<sup>1</sup> separate cerium in the quadrivalent condition from lanthanum and didymium by precipitation with powdered zinc oxide, and then separate lanthanum from didymium by partially precipitating the hot concentrated solution with magnesia usta until the absorption bands of didymium have disappeared.

The effect of magnesium oxide as a precipitant was tried with a nearly saturated neutral solution of the chlorides of these yttrium earths ( $R^{III} = 104.4$ ). Muthmann states that he stopped the precipitation when the didymium absorption bands had just disappeared. The authors found, however, that while a precipitate formed easily it would not settle sufficiently to enable the absorption bands to be observed.

The solution of the chlorides was heated to boiling, and while in vigorous ebullition, powdered magnesia was added in small quantities, with constant stirring. The precipitate which soon separated was first washed by decantation and was then washed upon a filter with hot water. The mother-liquor and the four wash-waters were evaporated nearly to saturation and the precipitation was repeated. A second repetition of this procedure gave a third fraction and the mother-liquor and wash-waters from this were then precipitated with oxalic acid for the fourth and final fraction.

Each of the precipitates was dissolved in hydrochloric acid and the solution was concentrated. These four solutions showed practically no variations in absorption bands when examined with a direct vision spectroscope. The solution from the first precipitate was treated with ammonium chloride and ammonium oxalate as Muthmann recommends, and the resulting precipitate was washed by decantation with hot water containing 0.1 per cent. hydrochloric acid and was then washed with water alone. The precipitate was free from magnesia but contained iron. The oxalates were at first non-crystalline and settled very slowly, but the

<sup>1</sup> *Ber. d. chem. Ges.*, 31, 1719.

addition of the dilute acid caused them to separate in crystalline condition. It was found that, by adding oxalic acid to the neutral chloride solution of these precipitates, complete precipitation of the rare earths could be obtained and this precipitate was free from magnesia, provided ammonium chloride was present. This method of purification was therefore used with the other fractions. The oxalates from all four of the fractions were ignited and dissolved in hydrochloric acid. Since the resulting solution contained traces of iron, portions of each fraction were freed from iron by reprecipitation with oxalic acid, and the atomic weight determinations were made with this purified material. The atomic weights and absorption spectra showed that very little change had been caused in the earth mixture by fractional precipitation with magnesium oxide.

#### TREATMENT WITH POTASSIUM TRINITRIDE, $\text{KN}_3$ .

The method proposed by Dennis and Kortright<sup>1</sup> for the separation of thorium from members of the cerium and yttrium groups, by means of potassium trinitride, was tried to see if perhaps some reaction similar to the one for thorium could be found. The results were entirely negative. Partial precipitation by potassium trinitride was found to fraction the rare earths of this group rather slowly. The precipitate in the case of thorium was thorium hydroxide. In this case it seemed rather to be a basic nitrate. It was white, very finely divided, and adhered to the beaker, and had also a tendency to go through the filter.

A dilute solution of the nitrate ( $R^{\text{III}} = 112.16$ ) was treated with a dilute solution of potassium trinitride containing free hydronitric acid and boiled. A precipitate was obtained on boiling for two or three minutes. It was filtered, washed with hot water, dissolved in nitric acid and converted into oxalates. The atomic weight was 118.96. The nitric acid solution was pink, and the absorption bands were practically the same as in the original solution.

#### FRACTIONAL PRECIPITATION WITH AMMONIA.

The work of many chemists who have investigated the earths of the yttrium group has shown that these elements can unquestionably be partially separated by a long series of fractions with dilute ammonium hydroxide, but the work is so extremely tedious

<sup>1</sup> *Ztschr. anorg. Chem.*, 6, 35.

and the separations are so very slow that it is questionable whether this procedure can be considered to be of material value. As an illustration of the slight effect of fractionation by this reagent one experiment will suffice.

A very dilute solution of the neutral chlorides containing about 57 grams of the oxides in 12 liters was treated with an amount of dilute ammonia sufficient to precipitate only one-tenth of the earths present. During the addition of the ammonia the solution was vigorously stirred by blowing through it a blast of air and this stirring was continued for about an hour. A precipitate formed very slowly. The hydroxides were then washed by decantation until the wash-water gave no precipitation with ammonia. The mother-liquor and wash-waters were evaporated to the original volume and precipitated again with the same amount of ammonia. The atomic weights of the earths precipitated in these two treatments were 103.9 and 104.0, while that of the original material was 96.

#### FRACTIONATION WITH AMMONIUM CARBONATE AND DILUTE ACETIC ACID.

Mosander<sup>1</sup> in 1843 mentioned that the hydroxides of the rare earths of this group are soluble in a concentrated solution of ammonium carbonate and that they could be fractioned in this way. Krüss<sup>2</sup> also mentioned this solubility.

This treatment alone was first tried here. The results were much better than was expected. The rare earth hydroxides were precipitated by ammonia (the latter need not be washed out). By a single treatment of these hydroxides with a quantity of a saturated solution of ammonium carbonate sufficient to dissolve one-fourth of the whole, an earth mixture was dissolved whose metal atomic weight was 121.41. The bases in the undissolved portion had an atomic weight of 107.94, while the original solution contained a metal mixture of atomic weight 108.08.

Quantities of saturated ammonium carbonate solution sufficient to dissolve other amounts of the precipitated hydroxides than one-fourth were then tried on different portions of this earth-mixture. An amount of carbonate solution sufficient to dissolve one-tenth of the hydroxides precipitated was added to one portion, while to others were added amounts of the carbonate solu-

<sup>1</sup> *Phil. Mag.*, 23, 251; *Ann. Chem.* (Liebig), 48, 219.

<sup>2</sup> *Ann. Chem.* (Liebig), 265, 1.



tion sufficient to dissolve nine-tenths, one-fifth, one-third, and one-half. On the whole, however, the addition of one-fourth or perhaps one-fifth the amount of carbonate solution necessary to dissolve all the hydroxides seems to be most suitable for this method of fractionation. The total precipitation of the earths by a solution of ammonium carbonate with partial solution of the precipitate in an excess of that reagent was also tried, but this is no better than precipitation with ammonia and partial solution in ammonium carbonate. A second extraction of the hydroxides from the undissolved portion ( $R^{III} = 107.94$ ) from the first treatment was made, and the atomic weight of the metal mixture which dissolved was 125.91. Evidently the material could be thus extracted at least twice with profit.

To the dissolved portion mentioned above ( $R^{III} = 121.41$ ) there was then added very dilute acetic acid (1 : 30) slowly and with constant stirring, first adding concentrated acetic acid just to turbidity. This treatment had a most marked effect. The granular precipitate thrown out was of a pink color and when dissolved showed all the absorption bands very strongly, while the bands in the remaining solution were much weakened.

When the dilute acetic acid had been added as above, a point was reached at which the addition of more acid would produce no further precipitate. This is due to the fact that the rare earth hydroxides of this group are nearly as soluble in ammonium acetate as in ammonium carbonate, and a state of equilibrium is soon reached between the three, after which dilute acetic acid has no effect upon the double ammonium salts of the rare earths. It was necessary, when this point was reached, to filter, decompose the ammonium carbonate solution with hydrochloric acid, dissolve the precipitate which was formed by further addition of the acid, and then to precipitate the whole with ammonia, wash, redissolve in hydrochloric acid and reprecipitate with ammonia. The hydroxides were then dissolved in saturated ammonium carbonate solution and the precipitation by dilute acetic acid repeated.

This particular material after having been treated three times with ammonium carbonate and dilute acetic acid in the manner above described, gave a very small amount (less than 1 gram) of an earth which yielded a white oxalate and a white oxide. A determination, not in duplicate, of its metal atomic weight gave the interesting result of 170. In the dry oxide only, the green ab-

sorption band of erbium was visible by reflected light. In saturated solution this earth mixture did not show the absorption bands of holmium, thulium, nor dysprosium, but those of erbium and samarium were visible. They were, however, much weaker than in the original solution. The spark spectrum of this solution was also examined, and the following lines of ytterbium as given by 'Thalén' were found :

Angle.	Wave-length.	Thalén's measurements.
10° 57' 00"	6220.9	6221.0 (1)
9° 46' 00"	5555.6	5555.5 (1)
9° 37' 30"	5475.7	5476.0 (1)
9° 24' 30"	5353.5	5352.0 (1)
9° 22' 30"	5334.8	5334.0 (1)
9° 18' 50"	5300.3	5300.0 (4)
8° 24' 10"	4785.7	4785.5 (2)
8° 17' 40"	4724.5	4725.0 (2)

The spark spectra of erbium and samarium were very weak. None of the characteristic gadolinium lines were found. The mixture was, therefore, ytterbium and erbium with some samarium, but no holmium, thulium, or dysprosium, no yttrium, gadolinium, or terbium.

To show further the effectiveness of this method of fractionation, it was tried on nearly all of the material in hand. The material was divided into two parts, in one of which the bases had an atomic weight of 117.37 and in the other of 107.15. Each of these portions was carefully purified by treating the boiling, slightly acid chloride solution with hydrogen sulphide, filtering, boiling to expel hydrogen sulphide, then precipitating with ammonia and washing, dissolving the precipitate in dilute hydrochloric acid, neutralizing and precipitating with oxalic acid solution, stirring the while by blowing air through the solution. The oxalate precipitate was washed with 0.1 per cent. hydrochloric acid to remove iron, then with water, dried, ignited, and dissolved in hydrochloric acid. The atomic weights given above were obtained from the material thus purified by precipitating this chloride solution again with oxalic acid, both solutions being boiling hot.

The details of the treatment for the solution ( $R^{III} = 117.37$ ) were as follows: The chloride solution was divided and placed in three tall cylinders, diluted and precipitated with ammonia.

<sup>1</sup> *J. de Phys.*, (2), 2, 37.

The hydroxides were washed, then dissolved completely in saturated ammonium carbonate solution, and concentrated acetic acid added just to turbidity. Then to each of the three cylinders was added 1000 cc. of dilute acetic acid (1 part acid diluted to 30 with water) in small quantities at a time and with constant stirring by a current of air. The flocculent precipitate soon became granular and could easily be separated from the mother-liquor by decantation. The last of the mother-liquor was removed from this fraction 1 by suction. Dilution with water caused the earths to precipitate from the ammonium carbonate solution; therefore the mother-liquor could not be washed out. The mother-liquors were treated with concentrated hydrochloric acid till the ammonium carbonate was destroyed and the resulting hydroxides dissolved, then precipitated with ammonia, dissolved in hydrochloric acid and reprecipitated with ammonia; then these hydroxides were treated again with saturated ammonium carbonate solution. This time the carbonate solution was placed in two cylinders, the excess of ammonium carbonate neutralized by concentrated acetic acid and 700 cc. of dilute acetic acid added to each one slowly and with constant stirring. The precipitate was fraction 2.

The mother-liquors here were removed and decomposed exactly as before, and the ammonium carbonate solution of the hydroxides neutralized with concentrated acetic acid and treated in one cylinder with about 600 cc. of dilute acetic acid (fraction 3). The mother-liquor from this fraction still showing a trace of the erbium band in the green after its conversion by the usual decomposition into chloride solution and concentration, it was diluted, precipitated with ammonia, dissolved in saturated ammonium carbonate solution as before and precipitated this time after neutralization by about 30 cc. of dilute acetic acid. The precipitate (fraction 4) was, of course, slight. The mother-liquor from it was dissolved in hydrochloric acid, nearly neutralized with ammonia and precipitated with oxalic acid to remove most of the iron. The oxalates were washed, dried, ignited, and dissolved in hydrochloric acid. This solution concentrated to saturation gave three absorption bands, the red and the green of erbium, and the samarium band between the blue and the green, none of them strongly. The atomic weights of the bases for the series were :

Original, 117.37.				
1	2	3	4	Residual mother-liquor.
115.25	116.33	141.62	159.78	165.48

The other material ( $R = 107.15$ ) treated in the same manner yielded the following series of atomic weights :

1	2	3	4	Residual mother-liquor.
105.33	102.4	110.6	119.45	146.53

It is worthy of note here that the metal atomic weights of the first two of the fractions in each of these series are quite close together, while those of the other fractions show a marked divergence from one another. In the second series the curve of atomic weights even goes through a minimum. There are two reasons for the apparent non-fractionation in these first two fractions. One is that the larger portion of the material used was precipitated in these first two fractions. The other and more important one is that the erbium ( $R^{III} = 166$ ), terbium ( $R^{III} = 159$ ), and yttrium ( $R^{III} = 89$ ) have so distributed themselves in the first and second fractions more terbium in the first, more erbium in the second, that the atomic weights of the metal mixtures are about the same.

The changes in color of the ignited oxides from these series were very marked. In the first series the original earth was a deep orange-yellow color. No. 1 gave a more deeply colored earth, No. 2 was chamois-colored, No. 3 pink, No. 4 white with a pinkish cast, and the earth from the mother-liquor almost white. In the second series the earth from the original solution had a deeper orange-yellow color than that from the other original solution. No. 1 was more deeply colored yet than this original solution, No. 2 lighter, No. 3 chamois-colored, No. 4 the same, and that from the mother-liquor white with a pinkish cast.

This color change evidences a marked change in the terbium content of the various fractions. Terbium concentrates very markedly in the first fractions. It is true that much the larger portion of the earths was thrown out in the first fraction in these two series, but by a short systematic fractionation, erbium material can unquestionably be obtained terbium-free.

This method seems then to offer a method for the comparatively rapid concentration of terbium with yttrium at one end of the series, and of erbium and ytterbium at the other. Holmium, thulium, and dysprosium concentrate in the middle fractions.

The results thus far obtained in this investigation may be briefly summarized as follows :

The Gibbs method of determining the equivalent weight does not give exact results even when the conditions prevailing in different series of determinations are identical.

There is a slight error in the sulphate method of determining the equivalent weights, due to the formation of some acid sulphate.

Of the many methods of partial precipitation which were investigated the following seem to be the most rapid : primary potassium oxalate, potassium trinitride, partial decomposition by fusion of the nitrates with alkali nitrates, and electrolysis of neutral solutions. Magnesia usta causes fractionation of this material, but the progress of the separation can not be easily controlled with the spectroscope as was done by Muthmann in his work on didymium.

One of the best methods for the separation of yttria from the other members of this group is that of fractional precipitation of a neutral solution by potassium chromate. Quite pure yttria may be obtained in this manner at the end of a comparatively short series of fractions.

Unusually rapid separation of the earths of this group is effected by ammonium carbonate and acetic acid. Fractional solution of the hydroxides by means of a saturated ammonium carbonate solution causes quite rapid separation, and if this ammonium carbonate solution be fractionally precipitated by addition of acetic acid, the results are most striking. Ytterbium is the last of the earths to be precipitated by this treatment. Erbium and terbium concentrate in the first fraction..

CORNELL UNIVERSITY,  
January, 1902.

---

## ELECTROLYTIC DEPOSITION OF LEAD FROM A PHOSPHORIC ACID SOLUTION.

BY A. F. LINN.

Received January 20, 1902.

**L** EAD has been successfully deposited as metal, by the electric current, from a solution of the double oxalate, the acetate, the oxide in sodium hydroxide, and also the phosphate dissolved in the latter reagent.<sup>1</sup> From each of these solutions the separa-

<sup>1</sup> Smith's "Electrochemical Analysis," p. 62.

tion of metal is complete and satisfactory, but the results are almost invariably too high, owing to the tendency of the moist deposit to undergo partial oxidation.

Smith therefore recommends the employment of a nitric acid solution containing from 10 to 20 per cent. of free acid, from which the lead separates as dioxide upon the anode. Some interesting results have been obtained by Smith<sup>1</sup> in the electrolysis of metallic phosphates in acid solution, but as far as the writer is aware, no experiments are recorded showing the deportment of lead toward the current in the presence of an excess of phosphoric acid. Preliminary trials showed that the metal could be deposited from a solution of this kind completely, and in such a form as to warrant a more extended study. The phosphoric acid used had a specific gravity of 1.71. In an excess of acid of this strength lead phosphate, precipitated either by disodium hydrogen phosphate or phosphoric acid, is readily soluble. With such a solution the following experiments were made.

The method of working was to take a definite volume of lead nitrate solution, precipitate the phosphate by disodium hydrogen phosphate or phosphoric acid, dissolve this in an excess of the phosphoric acid, and then electrolyze by a current of known strength. The deposited metal was washed with freshly boiled distilled water, absolute alcohol and ether, and finally dried in an air-bath at 100°–110° C. The deposition of metal took place at ordinary temperatures.

From a solution, prepared by precipitating lead phosphate by phosphoric acid, and then dissolving this in an excess of the precipitant, the lead separates in a partly crystalline and partly spongy condition, but sufficiently adherent to allow of thorough washing. If the amount of lead in the solution is too great, or the current too strong, the deposit is always very spongy and some of it is apt to be carried away in the washings.

On the other hand, from a solution made by adding more than enough disodium hydrogen phosphate for complete precipitation of lead phosphate, and then dissolving this in an excess of phosphoric acid, the lead deposit forms on the platinum dish a smooth, uniform, gray coating similar to that produced from an alkaline solution of lead. In a few experiments some brown discolorations were noticed on the dried deposit. These were taken to indicate

<sup>1</sup> *Am. Chem. J.*, 12, 329, and 13, 206.

oxidation. Throughout the course of this work the tendency of the deposit to oxidize in the drying process did not give much difficulty, if after a thorough washing with ether the latter is evaporated by the heat of the hand before the crucible or dish is placed in the air-bath.

The greatest difficulty encountered was the readiness with which the moist deposit dissolved in the wash-water after the current was interrupted. After a number of trials it was found best to allow the current to act during the washing with water, then to *very rapidly* wash with a small amount of absolute alcohol, and finally with ether as stated above.

When a strong current was used, or even in the case of a weaker current allowed to act for a longer period than is required for the complete deposition of the lead, the deposit gave a test for phosphorus, and the platinum vessel in a number of experiments was found to be stained a light brown color after the solution of the deposited lead in warm moderately concentrated nitric acid. The brown stain seems to be insoluble in any single acid hot or cold. Preliminary tests show that it contains both lead and phosphorus. This substance, probably a phosphide of lead, is under examination at the present time.

Experiments 1-7 show that with a fairly strong current the lead separates in the spongy condition and is especially difficult to wash, without loss due to the solvent action of the wash-water. In No. 2 the lead deposit, after the first weighing, was allowed to stand in contact with 20 cc. distilled water for three minutes, then washed with alcohol and ether, dried and weighed again. The loss in weight was 2 mg., and the washings, which contained no solid particles mechanically removed, showed a strong test for lead with hydrogen sulphide.

In 9-12 the current acted for a much longer time than was required for complete deposition. In each case, the deposited lead when dissolved in moderately concentrated nitric acid gave a test for phosphorus, and the platinum dish showed the brown stains already mentioned.

Experiments 13-18 show that under the conditions given, lead can be deposited satisfactorily from a phosphoric acid solution. The results obtained would indicate that in a solution containing not more than one-tenth gram of lead, and to which about 10 cc. of sodium phosphate, and 12-14 cc. of phosphoric acid (sp. gr.

No.	Lead taken. Gram.	Lead found. Gram.	Diff. Per cent.	N.D. in Am- pere.	Volt- age.	Hra.	Dila- tion. cc.	H <sub>2</sub> PO <sub>4</sub> cc.	Na <sub>2</sub> H PO <sub>4</sub> cc.	Remarks.
1	0.0937	0.0912	- 2.6	0.018	3.5	2	130	..	..	Very spongy. Not all deposited by current.
2	0.0937	0.0917	- 2.1	0.018	3.5	4	130	10	10	Spongy. Precipitation complete. Pb found in washings by H <sub>2</sub> S.
3	0.0717	0.0700	- 1.8	0.018	3.5	7	130	10	10	Spongy. Precipitation complete. Pb found in washings by H <sub>2</sub> S.
4	0.0717	0.0730	+ 1.8	0.018	3.5	12	130	10	10	Spongy. Brown spots after drying.
5	0.0143	0.0150	+ 4.8	0.018	3.5	3	130	10	..	Spongy. Brown spots after drying.
6	0.0717	0.0711	- 8.3	0.018	3.5	3	130	10	..	Deposition complete. Pb found in washings by H <sub>2</sub> S.
7	0.1151	0.1148	- 0.26	0.018	3.5	4	130	10	..	Spongy but adherent. No test for Pb in washings.
8	0.0344	0.0369	+ 7.2	0.002	3	20	130	14	..	P in deposit.
9	0.0344	0.0340	- 1.1	0.011	3	5	130	14	..	Spongy. Pb found in washings.
10	0.0344	0.0356	+ 3.4	0.002	3	17	130	10	..	P in deposit.
11	0.0562	0.0575	+ 2.3	0.002	3	17	130	14	..	P in deposit.
12	0.0206	0.0205	- 0.48	0.002	3	4.5	130	10	8	Deposition complete.
13	0.0344	0.0342	- 0.58	0.003	3	5	130	7	5	Deposition complete.
14	0.0562	0.0560	- 0.35	0.002	3	7	130	12	10	Deposition complete.
15	0.0562	0.0561	- 0.17	0.002	3	6	130	12	8	Deposition complete. Washed with hydrant water. <sup>1</sup>
16	0.0937	0.0934	- 0.32	0.003	3	8	130	12	8	Deposition complete.
17	0.0937	0.0932	- 0.53	0.003	3	8	130	12	10	Deposition complete. Washed with hydrant water.
18	0.0562	0.0559	- 0.53	0.002	3	10	130	8	6	Deposition complete.

<sup>1</sup> Contains about 26 grains solids per gallon, consisting mainly of the carbonates of calcium and magnesium.



1.71), have been added, the metal can be quantitatively separated by a current having  $N.D._{100} = 0.003$  ampere, and voltage 3. The deposition is complete in twelve to fourteen hours.

#### SEPARATION OF LEAD FROM MANGANESE.

Phosphate of manganese is readily soluble in an excess of phosphoric acid. With such a solution several trials showed that even strong currents produced no effect other than to develop a pink coloration, suggesting the color of weak permanganate.<sup>1</sup> The current was allowed to act at ordinary temperatures for seventeen hours.

When lead and manganese were in the same solution and electrolyzed with

$N.D._{100} = 0.011$  ampere,

Voltage = 3,

Dilution = 130 cc.,

Phosphoric acid = 14 cc.

manganese dioxide was thrown out on the anode, while the lead deposit gave tests for both lead and manganese.

Further work is now being done to determine whether lead can be separated from manganese in a phosphoric acid solution.

WITTENBERG COLLEGE, SPRINGFIELD, O.,  
December 26, 1901.

---

[CONTRIBUTION FROM THE SHEFFIELD LABORATORY OF YALE UNIVERSITY.]

### RESEARCHES ON THIOCYANATES AND ISOTHIOCYANATES.

(THIRD PAPER.)

BY HENRY L. WHEELER AND HENRY F. MERRIAM.

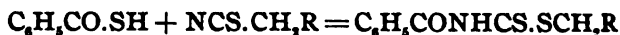
Received February 14, 1902.

[N our first paper<sup>1</sup> we described the results of an examination of rhodanides formed from certain alkylmonohalides and potassium thiocyanate, and showed that it is a simple matter to distinguish normal from isothiocyanates by their behavior with thiol acids.

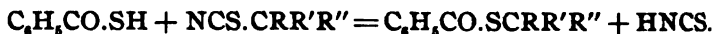
In the case of monothiocyanates, two reactions were observed. Either a direct addition was obtained with the formation of benzoyldithiourethanes, or along with other products, an ester of thiobenzoic acid resulted. The latter reaction was observed only in the case of certain secondary and tertiary thiocyanates:

<sup>1</sup> Smith: *Am. Chem. J.*, 12, No. 5.

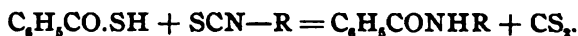
<sup>2</sup> This Journal, 23, 263 (1901).



and



On the other hand, isothiocyanates reacted smoothly to form benzamides and carbon disulphide:

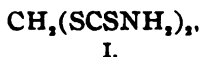


The work has now been extended to dirhodanides, and incidentally it has been found that not all dihalides yield dirhodanides.

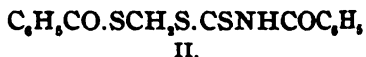
The dirhodanides which have been obtained from dihalides and potassium thiocyanate have, without exception, proved to be derivatives of normal thiocyanic acid.

We have found that the action of thiobenzoic acid, in the case of 1,1-dithiocyanates, as represented by methylene thiocyanate, and of 1,2-dithiocyan derivatives, ethylene and phenylethylene (styrolrhodanide), is by no means as smooth or simple as that in the cases previously described. In fact, even when the action was moderated by heating in the presence of benzene, thick oils or varnishes were invariably formed in addition to material that could be crystallized.

From methylene thiocyanate and thiobenzoic acid, three crystalline products were directly obtained. These, we have concluded, are methylene dithiourethane (I), benzoyldithiocarbamicmethylenethiolbenzoate (II), and the methylene derivative of benzoyldithiocarbamic acid (III):



I.



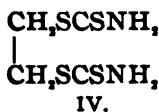
II.



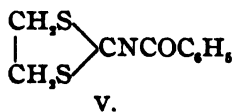
III.

During the reaction, hydrogen cyanide and carbon disulphide were formed, the latter being due to a secondary reaction of thiocyanic acid, HNCS.

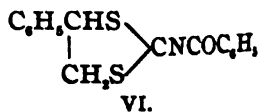
In the case of ethylene thiocyanate, we isolated two products. These were ethylene dithiocarbamate (IV), and the benzoyl-derivative of imidomethyleneethylene disulphide (V), while phenylethylene gave the corresponding imidomethylenephényl-ethylene disulphide (VI):



IV.



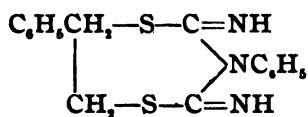
V.



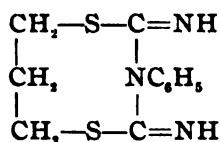
VI.

As an example of a 1,3-dithiocyanate, trimethylene rhodanide was examined. This reacted in the normal manner for a primary thiocyanate, and a bisdithiourethane was smoothly formed.

A property which appears to be unique for normal thiocyanates was observed in the case of trimethylene and phenylethylene thiocyanates. These compounds combine directly with one molecular proportion of aniline, probably to form seven- and eight-membered rings, the behavior being somewhat similar to that when pseudothiohydantoin is formed by the action of bases on ethylphenylthiocyanacetate, etc. The compounds may be viewed as cyclopseudophenyldithiobiurets. If tautomeric forms are excluded, two isomers are possible in the case of trimethylene thiocyanate, while from phenylethylene there are three. In the latter case, the end nitrogen atoms have different positions in respect to the phenyl group (VII). Since the trimethylene compound was not obtained from phenyldithiobiuret,  $C_6H_5NHCSNHCSNH_2$ , trimethylene bromide, and alkali or ammonia, it appears that the following formulas best represent the structure of these compounds :



VII.



VIII.

There seems to be no mention in the literature of dithiocyanates derived from 2,3-dihalides, and it is a noteworthy fact that such dihalides of this type, as we have examined, react with alcoholic solutions of potassium thiocyanate in a peculiar manner.

In each case, with the exception of isoeugenolmethyletherdibromide, the yellow, amorphous material or mixture called pseudocyanogen sulphide<sup>1</sup> was formed in more or less amount. In these cases, the halides act like free bromine on potassium thiocyanate.

In addition to pseudocyanogen sulphide, 2,3-dibrombutane,  $\text{CH}_3\text{CHBr}-\text{CHBr}-\text{CH}_3$ , gave a yellow oil. This was found to decompose on distilling under reduced pressure. The oil was, therefore, simply washed and then dried in a vacuum. A nitrogen determination gave 12.2 per cent., while the calculated for butylene dithiocyanate is 16.2 per cent. nitrogen. These figures

<sup>1</sup> Goldberg: *J. prakt. Chem.*, **64**, 166 (1901).

are given here merely to show that, in all probability, a dithiocyanate is formed in this case. Pinacone dibromide  $(\text{CH}_3)_2\text{CBrCBr}(\text{CH}_3)_2$ , and allylbenzene dibromide,  $\text{C}_6\text{H}_5\text{CHBrCHBrCH}_3$ , behaved in a similar manner.

2,4-Dinitrostilbene dibromide  $\text{C}_6\text{H}_3(\text{NO}_2)_2\text{CHBrCHBrC}_6\text{H}_3$ , dibromomethylhydrocinnamate,  $\text{C}_6\text{H}_5\text{CHBr-CHBrCO}_2\text{CH}_3$ , and the dibromide from the nitrile of phenylcinnamic acid,  $\text{C}_6\text{H}_5\text{CHBr-CBr}(\text{CN})\text{C}_6\text{H}_5$ , when warmed with alcoholic potassium thiocyanate gave abundant precipitates of pseudocyanogen sulphide. In these cases, the bromine was simply removed and the compounds were converted into the corresponding unsaturated products from which the bromides were prepared.

The property of forming pseudocyanogen sulphide is not confined to 2,3-dihalides, since it has been found that certain tertiary halides behave in like manner.

We have found that 1,2-dibromisobutane,  $(\text{CH}_3)_2\text{CBrCH}_2\text{Br}$ , gives pseudocyanogen sulphide. Monobrombenzylcyanide and bromcyanethyl acetate react in the same manner. Eugenol tetrabromide,  $\text{C}_6\text{H}(\text{OH.OCH}_2\text{Br})_2\text{CH}_2\text{CHBrCH}_2\text{Br}$ , gave no pseudocyanogen sulphide, nor did isoeugenol methyl ether dibromide,  $\text{C}_6\text{H}_2(\text{OCH}_3)_2\text{CHBr-CHBrCH}_3$ , a 2,3-dibromide. The exceptional behavior of the latter compound shows that the formation of pseudocyanogen sulphide is not general in the case of 2,3-dibromides. That this dibromide has the structure assigned to it, and that isoeugenol methyl ether does not add bromine in the 1,4 position, *i. e.*, part in the nucleus and part in the side-chain, has been proved by us by oxidation with potassium permanganate, whereupon veratric acid and dimethoxyphenylglyoxylic acid<sup>1</sup> were obtained.

#### EXPERIMENTAL PART.

*Methylene, Thiocyanate and Thiobenzoic Acid.*—Nineteen grams of the thiocyanate and 35 grams of the acid were dissolved in about two volumes of benzene and the mixture was heated on the steam-bath. After five or six hours it was found that yellow crystals had separated. Ten cc. of the benzene was then distilled off and found to contain hydrogen cyanide and carbon disulphide. The insoluble material, after washing with benzene, was crystallized from glacial acetic acid, whereupon, on slowly cooling, it separated in the form of small, slender, pointed, pale

<sup>1</sup> Ciamician and Silber: *Ber. d. chem. Ges.*, 23, 1164 (1890).

yellow prisms. It melted, not sharply and with effervescence, at 166°. The yield was about 4 grams, and on analysis the following results were obtained:

	Calculated for $C_5H_4N_2S_4$	I.	Found. II.
Nitrogen .....	14.1	14.2	13.9
Sulphur .....	64.6	65.5	...

The nitrogen determinations agree with the calculated for *methylene dithiocarbamate*,  $H_2NCS.SCH_2SCSNH_2$ , and this structure is confirmed by the fact that the compound dissolves in alkali and undergoes decomposition into methylene mercaptan and thiocyanic acid.

The benzene filtrate from the above was evaporated in a vacuum, and the thick oil thus obtained was stirred with ether containing a little alcohol. The solid material, thus produced, was crystallized from alcohol and benzene, whereupon yellow elongated plates melting at 138°–139° were obtained. The yield was about 4 to 5 grams, and analysis gave the following results:

	Calculated for $C_{16}H_{18}O_2NS_2$	I.	Found. II.
Nitrogen .....	4.03	4.33	4.56
Sulphur .....	27.66	28.46	27.68

Since the material is soluble in alkali with decomposition and has a yellow color, the assumption that it contains a dithiourethane grouping seems justified. In view of the above analyses, this would then permit of the following structural formula:



The substance is, therefore, a *methylene ester of thiobenzoic and benzoyldithiocarbamic acids*.

The ether solution from the above was shaken with alkali and precipitated with carbon dioxide. The resulting oily solid was crystallized from benzene and ligroin, whereupon bright yellow crystals melting at 130°–131° were obtained. The yield, owing to decomposition by alkali, was less than a gram and a nitrogen determination gave:

	Calculated for $C_{17}H_{14}O_2N_2S_4$	Found.
Nitrogen .....	6.89	7.14

This corresponds to the calculated for, the methylene ester of benzoyldithiocarbamic acid,  $(C_6H_5CONHCS.S)_2CH_2$ .

*Methylene Thiolbenzoate*,  $(C_6H_5COS)_2CH_2$ .—The possibility

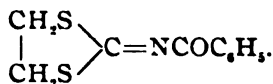
suggested itself that the solubility of the above compounds in alkali might be due to the presence of two negative groups attached to methylene and not to a dithiourethane group. In order to decide this point, we have prepared the methylene ester of thiolbenzoic acid by treating potassium thiolbenzoate with methylene iodide. The mixture in alcoholic solution reacted at once, and the product formed long, snow-white needles melting at  $120^{\circ}$ . It is insoluble in, and remains unaffected by dilute alkali. A sulphur determination gave:

	$C_{15}H_{12}O_2S_2$	Found.
Sulphur.....	22.22	22.31

*Ethylene Thiocyanate and Thiobenzoic Acid.*—Thirty grams of ethylene thiocyanate were heated on the steam-bath, for six to eight hours with 56 grams of thiobenzoic acid, diluted with 125 cc. of benzene, whereupon it was found that a crystalline precipitate had separated. About 10 cc. of the benzene were then distilled off, and this gave the reactions for carbon disulphide and hydrogen cyanide. The insoluble material was crystallized from glacial acetic acid and, on slowly cooling, it came down in aggregations of flattened prisms, of a very pale cream color. Thirteen grams of this material were obtained melting, not sharply, at  $188^{\circ}$ – $189^{\circ}$ . The analytical results were as follows:

	Calculated for $C_4H_4N_2S_4$	Found.
Carbon .....	22.6	22.2
Hydrogen.....	3.8	3.6
Nitrogen ....	13.2	13.7

Since the material, on treating with alkali, is smoothly decomposed into ethylene mercaptan and thiocyanic acid it follows that the substance is *ethylene dithiocarbamate*,  $H_2NCS.SCH_2CH_2S.CS.NH_2$ . The second product was obtained by partly evaporating the benzene from the above filtrate, whereupon beautiful, colorless prismatic tables separated. These were crystallized from alcohol and benzene, and melted then at  $80^{\circ}$ – $81^{\circ}$ . The yield was 20 grams and a nitrogen determination agreed with the calculated for *benzoylimidomethyleneethylene disulphide*,



	Calculated for $C_{10}H_8ONS_2$	Found.
Nitrogen.....	6.27	6.24

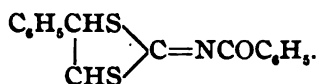
The structure of this compound was proved by preparing it from the so-called rhodanethylsulfin hydrochloride<sup>1</sup> and benzoyl chloride by means of the Schotten-Baumann reaction. The two products were identical in every respect. This excludes the possibility that the compound prepared by Miolati, melting at 141°–143°, is, as he supposed, benzoylimidomethyleneethylene disulphide.

When the material was treated with aqueous alkali it remained insoluble and apparently unaffected. With strong alcoholic potash it readily dissolved and was decomposed into ethylene mercaptan, (ethylene tetrasulphide), thiocyanic acid, benzoic acid, and probably some ethylbenzoate.

*Chlorethylene Thiocyanate and Thiobenzoic Acid.*—When these substances were heated together on the steam-bath, in benzene solution, a white solid separated. This was crystallized from alcohol and ether. Colorless, thin, square plates were thus obtained which blackened about 200°, and melted with decomposition about 212°. This material is soluble in water and the solution gives a crystalline compound with stannous chloride. Its properties and the following nitrogen determination show that the substance is *imidomethyleneethylene disulphide hydrochloride*.

	Calculated for C <sub>8</sub> H <sub>6</sub> NCIS <sub>2</sub> .	Found.
Nitrogen .....	9.00	9.02

*Styrol thiocyanate and thiobenzoic acid*, in molecular quantities, were heated in benzene for a number of hours. The presence of carbon disulphide was then detected and, on evaporating some of the benzene, solid material was obtained. This crystallized from alcohol in thin plates and melted at 135°. The following analysis shows that this compound is *benzoylimidomethylenephényl-ethylene disulphide*,



	Calculated for C <sub>18</sub> H <sub>12</sub> ONS <sub>2</sub> .	Found.
Carbon .....	64.21	64.62
Hydrogen .....	4.34	4.85
Sulphur .....	21.40	22.27
Nitrogen .....	4.68	4.65

When this was warmed with alcoholic potash it decomposed,

<sup>1</sup> Miolati: *Ann. Chem.* (Liebig), 262, 61.

giving benzoic and thiocyanic acids. A colorless transparent varnish was also obtained but not further examined.

*Trimethylene Thiocyanate and Thiobenzoic Acid.*—Thirty grams of thiobenzoic acid and 17 grams of trimethylene thiocyanate were diluted with 50 cc. of benzene and heated on the steam-bath for ten hours. Ten cc. of the benzene were then distilled off, and the fact that carbon disulphide and hydrogen cyanide were present was established. On allowing the reaction product to cool, a yellow crystalline mass was obtained. This was crystallized from benzene and ligroin, whereupon it came down in long slender yellow prisms melting at  $154^{\circ}$ – $155^{\circ}$ . The yield was about 30 grams. It was soluble in aqueous alkali and was precipitated with more or less decomposition by carbon dioxide. A nitrogen determination gave:

	Calculated for $C_{10}H_{10}O_2N_2S_4$	Found.
Nitrogen.....	6.45	6.39

This is, therefore, *trimethylenebenzoyldithiocarbamate*,  $C_6H_5CO NHCS.SCH_2CH_2CH_2S.CSNHCOC_6H_5$ .

*Trimethylene Thiocyanate and Aniline.*—Five grams of trimethylene thiocyanate were heated with three grams of aniline, on the steam-bath, for twenty-four hours. The product was diluted slightly with alcohol, and then ether was added until no further precipitate was formed. On crystallizing from alcohol and ether, colorless transparent tables or prisms were obtained. These sintered at about  $168^{\circ}$  and melted at  $173^{\circ}$ . A nitrogen determination gave:

	Calculated for $C_{11}H_{13}N_2S_2$	Found.
Nitrogen.....	16.73	16.72

This result agrees with the calculated for, a *pseudomethylene-phenyldithiobiuret*. Attempts to prepare this from phenyldithiobiuret,  $C_6H_5NHCSNHCSNH_2$ , and alkali or sodium ethylate and trimethylene bromide gave only a yellow, extremely sticky varnish from which nothing was obtained in crystalline form. When aqueous ammonia was employed instead of alkali, a method used with success by Tursini<sup>1</sup> for the preparation of an ethyl derivative, the result was similar, except that in one case a very small amount of well-developed crystals were obtained, melting sharply at  $109^{\circ}$ .

*Styrol Thiocyanate and Aniline*, when heated on the water-bath

<sup>1</sup> Ber. d. chem. Ges., 17, 585 (1884).



in molecular proportions, gave a gummy mass. This was dissolved in a little alcohol, and ether added until no more solid was precipitated. On crystallizing from a mixture of alcohol and ether, colorless plates, melting at  $205^{\circ}$ , were obtained. The analysis showed that this material is a *pseudophenylethylenephenyldithiobiuret*:

	Calculated for $C_{16}H_{16}N_2S_2$ .	Found.
Nitrogen.....	13.41	13.32
Sulphur .....	20.45	21.07

*Metaxylylene Thiocyanate*,  $C_8H_4(CH_2SCN)_2$ , from metaxylylene bromide and potassium thiocyanate, forms colorless prisms, when crystallized from alcohol, melting at  $160^{\circ}$ – $161^{\circ}$ . A nitrogen determination gave:

	Calculated for $C_{10}H_8N_2S_2$ .	Found.
Nitrogen.....	12.72	12.74

The crude product of the action of thiobenzoic acid on this substance was a varnish from which nothing solid was obtained. Thiobenzoic acid both with 1,2-propylene dithiocyanate, and 1,2,3-tripropylene thiocyanate also gave thick oils which were not further examined.

*Benzal chloride and potassium thiocyanate*, in alcoholic solution, gave a mixture of benzaldehyde and ethyl thiocyanate.

*Methyldibromhydrocinnamate and Potassium Thiocyanate*.—In the introduction it was mentioned that certain 2,3-dibromides react with potassium thiocyanate with the removal of bromine and formation of unsaturated compounds along with pseudocyanogensulphide. This peculiar reaction is well illustrated by the behavior of the dibromide obtained by adding bromine to methylcinnamate. Fifty grams of the dibromide were heated for eight hours with 40 grams of potassium thiocyanate, and 60 cc. of alcohol. In fact on simply mixing in the cold a yellow precipitate formed at once. This was extracted with water, alcohol, and carbon disulphide and then a nitrogen determination gave 24.65 per cent., while the analyses of various pseudocyanogen sulphide preparations, made by Goldberg, gave 22 to 27 per cent. nitrogen. On the other hand isopersulphocyanic acid contains 18.6 per cent. nitrogen.

The alcoholic solution was evaporated and the residue washed and taken up in petroleum ether, which left a small amount of substance undissolved. On evaporating, crystals sep-

arated melting at  $33^{\circ}$ , the melting-point of methyl cinnamate. This product was then distilled, and the boiling-point also agreed with that of methyl cinnamate. The yield after all this treatment was found to be 15 grams or 60 per cent. of the calculated.

The *dibromide from 2,4-dinitrostilbene* (15 grams), when boiled with alcoholic potassium thiocyanate, gave 6 grams of pure 2,4-dinitrostilbene or 64 per cent. of the calculated.

The *dibromide from the nitrile of phenyl cinnamic acid* (60 grams) gave 24 grams of the unsaturated product or 70 per cent. of the calculated. These yields do not represent the total amount of unsaturated material formed, since no special effort was made to obtain the entire amounts.

NEW HAVEN, CONN.,  
February 10, 1902.

## LIQUID MIXTURES OF MINIMUM BOILING-POINT.

BY CLIFFORD D. HOLLEY.

Received January 24, 1902.

IN 1899, Dr. Garnett Ryland<sup>1</sup> reported the results of an investigation of 80 pairs of the more common liquids. He found that 45 furnished mixtures which distilled in the same proportions with a constant boiling-point below the boiling-points of the constituent liquids; one which presented no relative depression or elevation of the boiling-point; and 3 which were of an uncertain character. During the same year, E. F. Thayer<sup>2</sup> and J. K. Haywood<sup>3</sup> investigated several of the same mixtures, but instead of following the method of Ryland, and determining the minimum-point by repeated distillations, they determined the boiling-points of several mixtures of the liquid constituents, and plotted the resulting boiling-point curve. From a comparison of the two methods it is seen that the proportion in which two liquids give a minimum point on the boiling-point curve is the same in which they distil with a constant boiling-point which lies below that of either liquid constituent, and the boiling-points are the same in both cases. But little having been done along this line during the past two years, it seemed desirable to add to our knowledge of such phenomena, and continue the investigations of such systems as would be likely to furnish mixtures of minimum boiling-point.

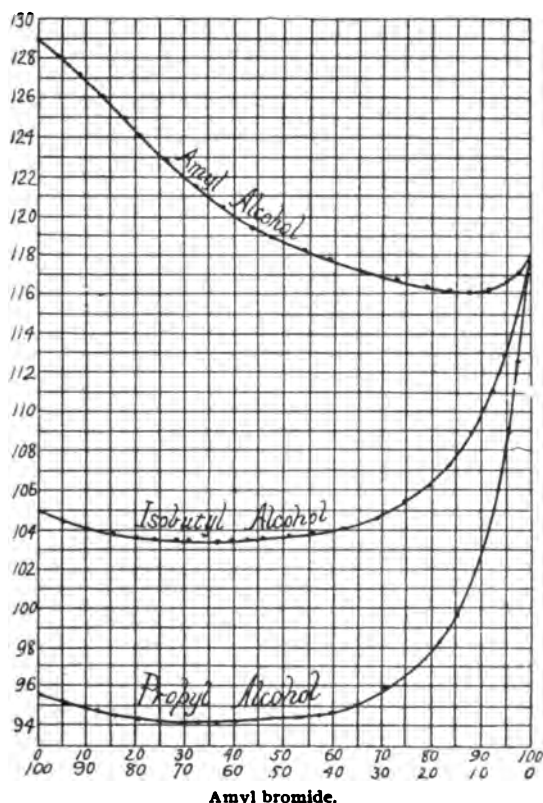
<sup>1</sup> *Am. Chem. J.*, 22, No. 5.

<sup>2</sup> *Jour. Phys. Chem.*, 2, 382; 3, 32.

<sup>3</sup> *Ibid.*, 2, 317.

In this paper are presented the results obtained with amyl compounds as one of the liquid constituents.

The boiling-point method was chosen as the more preferable, as in the distillation of bromides and iodides the formation of tarry residues towards the close of the distillation renders the thermometer readings inaccurate. A slightly modified form of Hite's apparatus was used. Instead of a differential thermometer,



one of the ordinary type was provided. It was graduated to fifths of a degree centigrade but with a scale so large that twentieths could be readily estimated.

A weighed amount of the lower boiling constituent was introduced into the bulb of Hite's apparatus, boiled for several minutes and the boiling-point and barometric pressure recorded. Weighed amounts of the other constituents were added, the successive boil-

ing-points noted, and this procedure was continued until the liquids were present in nearly equal proportions. The flask was then emptied and the process reversed, weighed portions of the first being added to a weighed amount of the second constituent. The results obtained are shown in the form of a plot. No corrections were applied to the curves because of variations of barometric pressure, as the error thus introduced is believed to be inappreciable. The liquids used were purified by redistillation, usually the first and last fourth being rejected. The portions reserved distilled at a very nearly uniform temperature.

In experimenting with mixtures of amyl iodide the bulb of Hite's apparatus was covered, and the investigation carried on in very subdued light, but even with these precautions the mixtures were noticeably colored towards the close of the operations from the separation of free iodine.

TABLE I.—AMYL BROMIDE AND AMYL ALCOHOL.

No.	Amyl bromide. Per cent.	Amyl alcohol. Per cent.	Temperature. C	Barometer. mm.
1	100.00	0.00	117.9	764.1
2	97.68	2.32	117.2	764.1
3	95.04	4.96	116.8	764.1
4	91.39	8.61	116.35	764.0
5	87.33	12.67	116.15	764.0
6	83.40	16.60	116.3	764.0
7	79.22	20.78	116.4	764.0
8	73.12	26.88	116.8	764.0
9	65.58	34.42	117.25	763.9
10	59.38	40.62	117.9	763.9
11	53.98	46.02	118.4	763.9
12	47.44	52.56	118.9	763.8
13	43.00	57.00	119.5	763.8
14	43.29	56.71	119.0	763.8
15	37.91	62.09	120.3	763.8
16	32.40	67.60	121.5	763.8
17	26.86	73.14	122.7	763.7
18	21.03	78.97	124.0	763.7
19	17.32	82.68	124.9	763.7
20	13.28	86.72	126.0	763.6
21	9.02	90.98	127.0	763.5
22	4.23	95.77	128.1	763.5
23	0.00	100.00	129.0	763.4

TABLE II.—ISOBUTYL ALCOHOL AND AMYL BROMIDE.

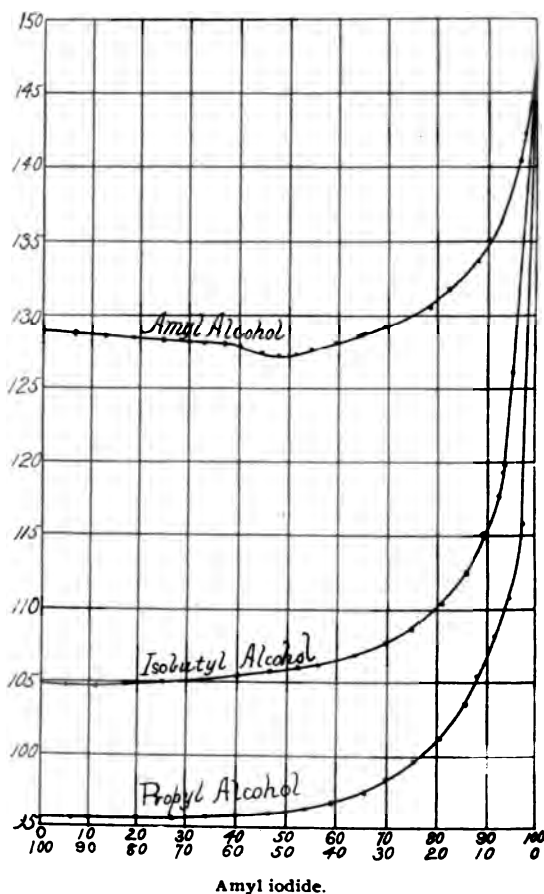
No.	Isobutyl alcohol. Per cent.	Amyl bromide. Per cent.	Temperature. °C.	Barometer. mm.
1	100.00	0.00	105.0	757.8
2	94.88	5.12	104.3	757.8
3	89.50	10.50	104.0	757.8
4	84.33	15.67	103.8	757.8
5	79.92	20.08	103.65	757.8
6	76.35	23.65	103.6	757.8
7	72.96	27.04	103.55	757.5
8	69.36	30.34	103.5	757.5
9	66.63	33.37	103.45	757.5
10	63.63	36.37	103.4	757.4
11	60.70	39.30	103.45	757.4
12	57.48	42.52	103.5	757.5
13	54.56	45.44	103.6	757.5
14	51.37	48.63	103.7	757.4
15	48.10	51.90	103.75	757.4
16	44.32	55.68	103.8	757.4
17	38.08	61.92	104.1	757.4
18	31.28	68.72	104.6	757.3
19	25.55	74.45	105.4	757.3
20	20.56	79.44	106.2	757.3
21	16.55	83.45	107.4	757.3
22	12.22	87.88	109.0	757.3
23	7.89	92.11	111.2	757.2
24	6.01	93.99	112.9	757.0
25	2.73	97.27	115.0	757.0
26	0.00	100.00	118.1	757.0

*Table I. Amyl Alcohol and Amyl Bromide.*—In the accompanying plot the left-hand ordinate represents 100 parts amyl alcohol. Amyl bromide (117.9°) and amyl alcohol (129.0° C.) furnish a mixture with a minimum boiling-point of 116.15° C. in the proportion of 12.7 parts amyl alcohol, and 87.3 parts amyl bromide. The minimum point is definitely defined. The first additions of amyl alcohol cause a rapid lowering of the boiling-point followed by a gradual rise until the maximum is reached. The curve exhibits a distinctly wavy tendency.

*Table II. Isobutyl Alcohol and Amyl Bromide.*—Isobutyl alcohol (105°) and amyl bromide (118.1°) in the proportion of 63.6 parts isobutyl alcohol to 36.4 parts amyl bromide, gives a mixture having a minimum boiling-point of 103.4° C. The major portion of the curve is very flat, and the minimum point is not sharply marked. From the curve it is seen that isobutyl alcohol can be diluted with amyl bromide until it contains nearly 43 per cent. of

the latter before the boiling-point of the mixture is raised above that of isobutyl alcohol.

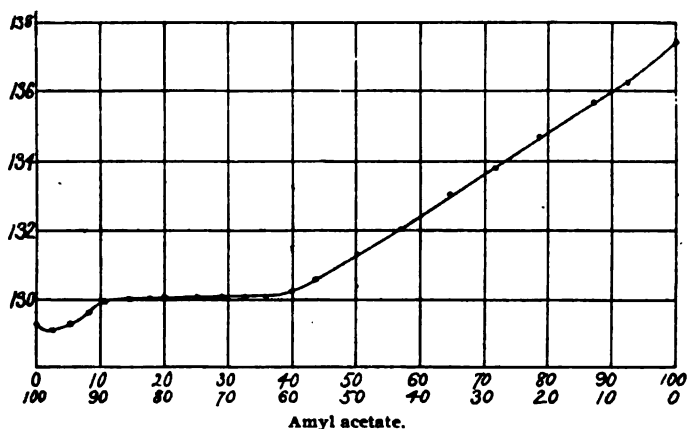
*Table III. Propyl Alcohol and Amyl Bromide.*—A mixture of propyl alcohol ( $95.5^{\circ}$ ), and amyl bromide ( $118.2^{\circ}$ ), in the proportions of 70.7 parts propyl alcohol to 29.3 parts amyl bromide, gives



a minimum point of  $94^{\circ}$ . The curve descends in a nearly straight line to the minimum, then rises very gradually at first, but at last with great abruptness to the maximum. Propyl alcohol may contain as much as 65 per cent. of amyl bromide without raising its boiling-point.

*Table IV. Amyl Alcohol and Amyl Iodide.*—Amyl alcohol

(128.9°) and amyl iodide (146.5°) furnish a mixture having a minimum boiling-point of 127.3° in the proportion of 52 parts amyl alcohol to 48 parts amyl iodide. The minimum point is



fairly well defined; the major portion of the curve is quite flat, and it is evident that amyl alcohol may contain as much as 65 per cent. of amyl iodide and still have a boiling-point below that of pure amyl alcohol.

TABLE III.—PROPYL ALCOHOL AND AMYL BROMIDE.

No.	Propyl alcohol. per cent.	Amyl bromide. per cent.	Temperature. °C.	Barometer, mm.
1	100.00	0.00	95.5	762.8
2	94.42	5.58	95.2	762.8
3	88.05	11.95	94.8	762.8
4	83.78	16.22	94.6	762.8
5	79.55	20.45	94.4	762.8
6	74.81	25.19	94.2	762.8
7	70.70	29.30	94.0	762.8
8	66.99	33.01	94.1	762.8
9	63.69	36.31	94.15	762.8
10	59.85	40.15	94.2	763.6
11	55.98	44.02	94.25	763.0
12	52.09	47.91	94.3	763.0
13	47.94	52.06	94.4	763.0
14	46.60	53.40	94.4	763.0
15	43.01	56.99	94.5	763.1
16	40.50	59.50	94.7	763.1
17	35.35	64.65	95.2	763.1
18	29.02	70.98	95.9	763.3
19	23.24	76.76	96.9	763.3

No.	Propyl alcohol. Per cent.	Amyl bromide. Per cent.	Temperature. °C.	Barometer. mm.
20	18.23	81.77	98.3	763.3
21	14.81	85.19	99.6	963.4
22	11.38	88.62	101.6	763.4
23	8.77	91.23	103.85	763.4
24	6.49	93.51	106.2	763.6
25	4.36	95.64	109.1	763.6
26	2.14	97.86	112.6	763.6
27	0.00	100.00	118.2	763.6

TABLE IV.—AMYL ALCOHOL AND AMYL IODIDE.

No.	Amyl alcohol. Per cent.	Amyl iodide. Per cent.	Temperature. °C.	Barometer. mm.
1	100.00	0.00	128.9	758.6
2	93.57	6.43	128.6	758.6
3	87.47	12.53	128.4	758.6
4	81.19	18.81	128.3	758.6
5	74.80	25.20	128.2	758.6
6	70.19	29.81	128.18	758.7
7	67.46	32.54	128.05	758.7
8	63.26	36.74	127.9	758.7
9	60.08	39.92	127.7	758.6
10	56.18	43.82	127.4	758.6
11	51.98	48.02	127.3	758.6
12	48.89	51.11	127.4	758.7
13	45.84	54.16	127.6	758.0
14	40.48	59.52	128.0	758.0
15	35.60	64.40	128.6	758.0
16	30.32	69.68	129.3	758.1
17	21.28	78.72	130.6	758.1
18	18.12	81.88	132.0	758.1
19	12.64	87.36	133.7	758.1
20	10.10	89.90	135.2	758.1
21	7.43	92.57	136.5	758.3
22	3.16	96.84	140.5	758.3
23	2.04	97.96	142.3	758.3
24	0.00	100.00	146.5	758.3

TABLE V.—ISOBUTYL ALCOHOL AND AMYL IODIDE.

No.	Isobutyl alcohol. Per cent.	Amyl iodide. Per cent.	Temperature. °C.	Barometer. mm.
1	100.00	0.00	104.8	747.4
2	94.88	5.12	104.7	747.4
3	83.36	11.64	104.7	747.4
4	82.35	17.65	104.8	747.3
5	74.99	25.01	105.0	747.5
6	67.56	32.44	105.3	747.5
7	59.67	40.33	105.5	747.5



No.	Isobutyl alcohol. Per cent.	Amyl iodide. Per cent.	Temperature. °C.	Barometer. mm.
8	53.87	46.13	105.8	747.5
9	47.88	52.12	106.1	747.5
10	43.40	56.60	106.2	747.5
11	36.86	63.14	106.9	747.8
12	29.92	70.08	107.8	747.8
13	25.39	74.61	108.7	747.8
14	19.20	80.80	110.4	747.8
15	14.48	85.52	112.6	747.8
16	11.00	89.00	115.0	747.8
17	7.73	92.27	117.8	748.0
18	5.26	94.74	121.0	748.0
19	2.32	97.68	126.0	748.0
20	0.00	100.00	146.5	748.1

*Table V. Isobutyl Alcohol and Amyl Iodide.*—Isobutyl (104.8°) alcohol and amyl iodide (146.5°) do not give a mixture having a definite minimum boiling-point. The first two additions of amyl iodide caused a lowering of the boiling-point of 0.1° C. This was followed by a gradual rise until the mixture contained about 70 per cent. of amyl iodide, when the boiling-point rose with great abruptness to the maximum.

TABLE VI.—PROPYL ALCOHOL AND AMYL IODIDE.

No.	Propyl alcohol. Per cent.	Amyl iodide. Per cent.	Temperature. °C.	Barometer. mm.
1	100.00	0.00	95.7	753.8
2	93.36	6.64	95.6	753.8
3	89.94	10.06	95.65	753.8
4	79.91	20.09	95.7	753.8
5	73.06	26.94	95.8	753.8
6	66.16	33.84	95.9	753.8
7	59.90	40.10	96.1	753.8
8	54.38	45.62	96.3	753.7
9	46.15	53.85	96.6	753.4
10	41.08	58.92	96.9	753.4
11	36.50	63.50	97.6	753.4
12	30.27	69.73	98.4	753.4
13	24.90	75.10	99.7	753.4
14	19.19	80.81	101.4	753.4
15	14.78	85.22	103.4	753.5
16	11.48	88.52	105.6	753.5
17	8.64	91.36	108.2	753.2
18	5.95	94.05	110.8	753.2
19	3.07	96.93	115.6	753.2
20	0.00	100.00	146.5	753.2

TABLE VII.—AMYL ALCOHOL AND AMYL ACETATE.

No.	Amyl alcohol. Per cent.	Amyl acetate. Per cent.	Temperature. °C.	Barometer. mm.
1	100.00	0.00	129.3	770.4
2	97.36	2.64	129.1	770.4
3	94.58	5.42	129.3	770.4
4	91.84	8.16	129.55	770.4
5	89.10	10.90	129.9	770.4
6	85.42	14.58	129.95	770.3
7	82.06	17.94	130.0	770.3
8	78.48	21.52	130.0	770.3
9	74.80	25.20	130.05	770.3
10	71.27	28.73	130.01	770.3
11	67.62	32.38	130.01	770.1
12	64.16	35.84	130.1	770.0
13	60.08	39.92	130.2	770.0
14	56.87	43.13	130.5	770.0
15	50.04	49.96	131.3	769.6
16	42.88	57.12	132.0	769.6
17	35.21	64.79	133.0	769.7
18	27.83	72.17	133.8	769.8
19	20.85	79.15	134.55	769.8
20	17.80	82.20	135.5	769.9
21	7.49	92.51	136.2	769.9
22	0.00	100.00	137.5	770.0

*Table VI. Propyl Alcohol and Amyl Iodide.*—Propyl alcohol (95.7°) and amyl iodide (146.5) give results very similar to those obtained with isobutyl alcohol and amyl iodide. There is a slight lowering of the boiling-point, 0.1°, by the first two additions of propyl alcohol. The major portion of the curve is slightly flatter than with isobutyl alcohol and the abrupt ascent to the maximum more marked.

*Table VII. Amyl Alcohol and Amyl Acetate.*—Amyl alcohol (129.3°) and amyl acetate (137.5°) give a mixture having a minimum boiling-point of 129.1° in the ratio of 97.4 parts amyl alcohol to 2.6 parts amyl acetate. A second determination was made, and the same result obtained. The curve exhibits some marked peculiarities. There is at first a slight lowering of the boiling-point followed by a corresponding rise; the curve then becomes perfectly flat until the mixture contains 40 per cent. amyl acetate, when the curve rises in a straight line to the maximum.

The following pairs of liquids were investigated, but no mixtures of minimum boiling-point were obtained:

Amyl alcohol 129°	and ethyl butyrate	120.6°
Amyl alcohol 129°	and bromoform	147.1°
Amyl acetate 137.5°	and ethylene bromide	129°
Amyl acetate 137.5°	and amyl bromide	118°
Amyl acetate 137.5°	and amyl iodide	146.5°
Amyl acetate 137.5°	and bromoform	147.1°
Amyl acetate 137.5°	and ethyl butyrate	120.6°
Amyl bromide 118°	and ethyl butyrate	120.6°
Amyl bromide 118°	and toluene	109.5°

Of the 16 pairs of liquids investigated, 5 gave mixtures having well-defined minimum boiling-points, while 2 showed no relative elevation or depression of the boiling-point.

The chemical constitution of the constituents exercises a greater influence in the formation of mixtures with minimum boiling-points than the close proximity of the boiling-points of the constituents. One constituent remaining the same, or with constituents closely related, mixtures with substances of similar chemical constitution yield similar boiling-point curves.

In the next paper the writer hopes to present the results obtained with propyl and isobutyl compounds.

UNIVERSITY OF MAINE.

---

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF MICHIGAN.]

## THE VOLUMETRIC ESTIMATION OF ALUMINA, AND FREE AND COMBINED SULPHURIC ACID IN ALUMS.

BY ALFRED H. WHITE.

Received January 29, 1902.

**I**N judging the quality of an alum, among the important determinations are those which give the amount of soluble alumina and the amount of sulphuric acid in combination with it or existing as free acid. The alumina may be satisfactorily estimated gravimetrically, but the method is tedious. A gravimetric estimation of the sulphuric acid gives not only that combined with aluminum plus that present as free sulphuric acid, but also that present as sodium sulphate, etc., and the amount of alkalis must be known before the amount of sulphuric acid combined with aluminum can be determined.

The determination of free sulphuric acid in alums by volumetric means has been repeatedly attempted. The hydrolysis of aluminum sulphate prevents direct titration with an alkali, since as fast as the free acid present is neutralized, more is formed by hydrol-

ysis, so that the solution will not remain neutral for an appreciable length of time until nearly all the acid originally combined with the aluminum has been neutralized, and most of the aluminum hydroxide precipitated. This cannot be made into a practicable quantitative method for the estimation of free and combined acid, as the formation of aluminate with alkaline reaction begins before all the hydroxide has been precipitated. Further if phenolphthalein is used as indicator the precipitated hydroxide obstinately holds, by adsorption, the pink color even when the solution is no longer alkaline so that the method, though perhaps giving in the hands of works chemists in constant practice results which are fairly concordant, is, because of these various errors, not to be considered a practicable analytical method. The following paper results from an attempt to work out a practicable method.

A standard solution of barium hydroxide was used instead of caustic soda to avoid any trouble caused by carbon dioxide in the caustic affecting the phenolphthalein used as indicator. It was found later that the barium hydroxide possessed other advantages. To prevent the adsorption of pink color by the precipitated aluminum hydroxide obscuring the end reaction, an addition of neutral potassium sodium tartrate (Rochelle salt) was made to hold the alumina in solution. The modification proved a good one. Duplicate results checked closely. There was no precipitation of alumina during the titration, nor even of barium sulphate. The solution remained perfectly clear and colorless until the end reaction, which was sharp. After standing a short time the solution became opalescent, and then milky, but no precipitate settled out. This marked retardation of the precipitation of barium sulphate was unexpected, and the conditions under which it occurs are undergoing further investigation.

To determine that the results thus obtained were accurate, a solution of aluminum sulphate was made by precipitating aluminum hydroxide from a solution of aluminum chloride with ammonia, washing the precipitate thoroughly and then dissolving in standard sulphuric acid which was afterward diluted to a liter (Solution A). The solution thus obtained was almost fifth-normal, and the amount of acid was slightly in excess of the amount theoretically necessary to form the normal aluminum sul-

phate. A duplicate solution of acid alone, carefully standardized gravimetrically, was used to check the results.

The method of procedure was as follows : To 25 cc. of the fifth-normal alum solution was added 50 cc. of 10 per cent. neutral potassium sodium tartrate, and the mixture was titrated cold with barium hydroxide solution, using phenolphthalein as indicator. This amount of tartrate was sufficient to prevent anything more than a slight opalescence in the solution before the end reaction. Duplicate titrations required 25.85 and 25.80 cc. of fifth-normal barium hydroxide. To determine the effect of the amount of tartrate, another titration was made, using 100 cc. of tartrate instead of 50. The amount of barium hydroxide solution used was 25.85 as before. The check solution of sulphuric acid required 25.65 cc. barium hydroxide, no difference being apparent whether no tartrate, 50 cc., or 100 cc. of tartrate were present. The solution containing the aluminum sulphate therefore requires slightly more barium hydroxide than that containing the sulphuric acid alone. A possible explanation is that the ionization of the barium hydroxide is lessened to such an extent by the aluminum tartrate complex that it requires an appreciably large excess of barium hydroxide to bring about the end reaction. If, however, the barium hydroxide is standardized against a solution of aluminum sulphate made from precipitated alumina and sulphuric acid as described, the results will be constant and give accurate results when extended to other alums. The addition of sodium sulphate in amount equivalent to the amount of sulphuric acid combined with the aluminum does not affect the result ; the addition of standard sulphuric acid increases the amount of barium hydroxide used by the theoretical amount. The addition of neutral tartrate and titration with barium hydroxide, therefore, affords an accurate method of determining the total sulphuric acid combined with the aluminum plus the excess of free acid, irrespective of the amount of sulphuric acid combined with alkalis.

As it is well known that the hydroxy-organic acids in general have the power of preventing the precipitation of alumina, salts of other acids than tartaric were tried, among them neutral sodium citrate. Sodium citrate prevented the precipitation of alumina, retarded the precipitation of barium sulphate, and

allowed a perfectly sharp end reaction, as did the tartrate, but the amount of barium hydroxide used was only a little over two-thirds of that required when titrating in the presence of the tartrate. Solution A, with neutral sodium citrate added, required only 17.95 cc. barium hydroxide instead of 25.84 when tartrate was used. Experiment showed that the addition of sodium sulphate did not affect the result and that an addition of standard sulphuric acid caused the theoretically calculated increase in the barium hydroxide used. It seemed that the result obtained when titrating in the presence of citrate could be due only to the formation of a complex aluminum ion and that this might furnish the basis of a method for the estimation of the aluminum. If we assume that the barium hydroxide used when titrating in presence of tartrate, represents free acid plus acid combined with alumina, while the barium hydroxide used when titrating in presence of citrate represents free acid, plus two-thirds of acid combined with alumina, the difference represents one-third of the sulphuric acid combined with the alumina, or one-third the alumina. In the above instance,  $25.84 - 17.95 = 7.89$  cc. fifth-normal barium hydroxide, and calculating the alumina on the assumption that this is equivalent to one-third of it we find that we get 0.0805 gram of alumina as compared with 0.0831 gram obtained gravimetrically. The volumetric result is too low. It seemed entirely possible that partial hydrolysis of the alum in the citrate solution might cause more barium hydroxide to be used than called for by the above supposition and that this might account for the low result. Accordingly, among other variations, the solution of aluminum sulphate was evaporated to dryness on the water-bath and dissolved in 50 cc. of 10 per cent. sodium citrate, and titrated. There were required only 17.58 cc. barium hydroxide instead of 17.95 cc., and the alumina calculated from this is 0.0842 gram instead of 0.0831 gram obtained gravimetrically. Using a saturated solution of citrate to redissolve the alum did not give an appreciably different result. Thus, the first method gives results considerably low while the second gives slightly high results. Some further experiments upon the influence of concentration and time follow, made upon a C. P. aluminum sulphate in a solution of 30 grams per liter (Solution B).

B.	Volume. Aluminum sulphate.	Water added.	Citrate added.	Barium hydroxide.	Remarks.
1	25	0	50	21.75	Titrated at once.
2	25	25	50	21.76	Titrated at once.
3	25	50	50	21.67	Water added; stood fifteen minutes; then citrate added, and titrated.
4	25	100	50	21.70	Water added; stood fifteen minutes; then citrate added, and titrated.
5	25	200	50	21.72	Water added; stood fifteen minutes; then citrate added, and titrated.
6	25	Evaporated to dryness and redissolved in 50 cc. 10 per cent. citrate; stood ten minutes before titrating; required 21.62 cc. barium hydroxide.			
7	0.750 gram (25 cc.) of solid salt, dissolved in 50 cc. 10 per cent. citrate and titrated at once, required 21.90 cc. barium hydroxide.				

The above series of experiments shows that the addition of varying amounts of water and variation of time within short intervals makes but slight difference in the result. The hydrolysis is apparently a slow one. In twenty-four hours, however, equilibrium is practically complete, as is shown by another series of experiments on a commercial aluminum sulphate dissolved to a strength of 30 grams per liter (Solution C).

C.	Volume. Aluminum sulphate.	20 per cent. ci- trate added.	Barium hydroxide.	Remarks.
1	25	25	21.0	Titrated at once.
2	25	25	21.02	Stood fifteen minutes before titrating.
3	25	25	20.62	Stood sixteen hours before titrating.
4	25	Evaporated to dry- ness and redis- solved in 50 cc. 10 per cent. ci- trate.	20.53	Titrated at once.
5	25		20.69	Stood ten minutes before titrating.
6	0.750 gram (25 cc.) solid salt dissolved in 50 cc. 10 per cent. citrate.		21.10	Stood ten minutes before titrating.

Nos. 3 and 5 show that if sufficient time is given to allow equilibrium to be established, the results are practically the same

whether the 50 cc. solution is evaporated to dryness and dissolved in 50 cc. of 10 per cent. citrate (20.69 cc.) or 25 cc. of solution are treated with 25 cc. of 20 per cent. citrate, and the solution allowed to stand sixteen hours (20.62 cc.). No. 6 in this series, as well as No. 7 in Series B, shows that the same result is not reached when dissolving the solid salt in citrate (B 7 = 21.90) and titrating as when evaporating to dryness, and redissolving in the same amount of citrate (B 6 = 21.62). Commercial alum is evidently not a homogeneous body, and further combination between the alumina or basic sulphate and the sulphuric acid takes place after solution in water.

The analytical method as finally worked out is as follows: Dissolve 3 grams of alum in 100 cc. of water. Take 25 cc. sample, add 50 cc. strictly neutral 10 per cent. potassium-sodium tartrate and titrate with fifth-normal barium hydroxide, using phenolphthalein as indicator. This is equivalent to the sulphuric acid combined with the alumina plus the free acid. Evaporate a duplicate 25 cc. sample to dryness on the water-bath, dissolve in 50 cc. strictly neutral 10 per cent. sodium citrate, allow to stand ten minutes and titrate with barium hydroxide, with phenolphthalein indicator as before. The difference between these results is equivalent to one-third of the sulphuric acid combined with the alumina and hence to one-third of the alumina. The barium hydroxide solution should be standardized by a blank determination upon a solution of sulphuric acid in which approximately enough precipitated aluminum hydroxide has been dissolved to correspond to aluminum sulphate. The aluminum hydroxide may be best made by precipitation of the chloride to insure absence of sulphate. Caustic soda, even when freed from carbon dioxide by barium hydroxide, does not give such satisfactory results as the barium hydroxide. As examples of the practicability of the method the following results on two widely differing alums are cited.

*Alum B, a C. P. aluminum sulphate:*

30 grams per liter (25 cc.) sample = 0.750 gram sample.

	cc.
Fifth-normal barium hydroxide for tartrate titration ...	$\left\{ \begin{array}{l} 32.50 \\ 32.55 \end{array} \right\}$ 32.52
Fifth-normal barium hydroxide for citrate titration....	$\left\{ \begin{array}{l} 21.60 \\ 21.63 \end{array} \right\}$ 21.62
Difference .....	10.90



$10.90 \times 3 = 32.70$  cc. fifth-normal barium hydroxide equals total sulphur trioxide theoretically necessary to combine with alumina, and therefore equals alumina.

$32.70 \times 0.003407 = 0.1114$  gram alumina equals 14.86 per cent. alumina. Alumina determined gravimetrically equals 14.73 and 14.80.

The close agreement between the figures 32.52 cc. (free and combined sulphur trioxide) and 32.70 cc. (combined sulphur trioxide) show that the alum is almost exactly neutral with an excess equal to 0.18 cc. of fifth-normal alumina.

*Alum C, a commercial aluminum sulphate :*

30 grams per liter (25 cc.) sample = 0.750 gram sample.

		cc.
Fifth-normal barium hydroxide for tartrate titration ...	$\left\{ \begin{array}{l} 33.59 \\ 33.59 \end{array} \right\}$	33.59
Fifth-normal barium hydroxide for citrate titration ....	$\left\{ \begin{array}{l} 20.64 \\ 20.74 \end{array} \right\}$	20.69

Difference ..... 12.90

$12.90 \times 3 = 38.70$  cc. fifth-normal barium hydroxide equals total sulphur trioxide theoretically necessary to combine with alumina and therefore equals alumina.

$38.70 \times 0.003407 = 0.1318$  gram alumina equals 17.58 per cent. alumina. Alumina determined gravimetrically equals 17.57 and 17.50.

$38.70 - 33.59 = 5.11$  cc. fifth-normal alumina equals 0.0174 gram alumina equals 2.32 per cent. alumina more than is sufficient to form aluminum sulphate.

Alum B, as shown by the above figures, is slightly basic, but a determination of free acid by the method of Beilstein and Grosset<sup>1</sup> gave 0.9 per cent free acid. This method of Beilstein and Grosset has been investigated by V. Keler and Lunge,<sup>2</sup> who state that it gives results which are uniformly slightly high but otherwise very accurate, and it therefore became necessary to explain the discrepancy. The method of Beilstein and Grosset is as follows: Dissolve 1 or 2 grams of alum in 5 cc. of cold water, add 5 cc. of a cold, saturated solution of ammonium sulphate, allow to stand, with frequent stirring, for fifteen minutes, and then add 50 cc. 95 per cent. alcohol. Filter, wash with 50 cc. 95 per cent. alcohol, evaporate to dryness on water-bath, dissolve in water, and titrate with tenth-normal potassium hydroxide, using litmus as indicator. All the alum is, in this process, supposed to be precipitated as normal ammonium alum together with most of the excess ammonium sulphate, and the free sulphuric acid re-

<sup>1</sup> Bulletin de l'Academie Imperiale des Sciences in St. Petersburg, 1890, p. 147.

<sup>2</sup> Ztschr. angew. Chem. (1894), p. 669.

mains in solution together with a small amount of ammonium sulphate. Three determinations of free acid in alum B by this method gave 0.86, 0.88, and 0.89 per cent. free acid as sulphur trioxide—as good an agreement as could be desired. To test whether an error in Beilstein and Grosset's method due to hydrolysis might not be responsible for this apparent free acid, variations were made in amount of water and concentration of sulphur trioxide, with the following results:

Sample. Grams.	Water. cc.	Saturated solution (NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> . cc.	Alcohol. Per cent.	Free acid as SO <sub>3</sub> . Per cent.
2	10	10	95	0.96
3	10	10	95	0.88
3	5	10	absolute	0.70
3	5	5 + 5 gram solid ammonium sulphate.	absolute	0.61

Blank determinations showed that the change in results was not due to impurities in the ammonium sulphate or alcohol. The results show that the decrease in the relative amount of water decreases the apparent amount of free acid, but although hydrolysis does thus play a part in influencing the results, there remains as the lowest figure, 0.6 per cent., which can hardly be attributed to an error in the method. Turning back to the series of results obtained by titrating alum B in presence of citrate, it was remarked that the figures obtained by dissolving the alum directly in citrate were higher than those obtained by dissolving the alum in water, then evaporating to dryness and redissolving in citrate which showed a greater amount of free acid in the original alum than after evaporation to dryness. If the results in B 7 are taken and calculation made we find that there are required

Fifth-normal barium hydroxide for tartrate titration . . . . .	cc.
Fifth-normal barium hydroxide for citrate titration when alum dissolved directly in citrate . . . . .	32.52 21.90

Difference . . . . . 10.62

$$10.62 \times 3 = 31.86 \text{ cc.}$$

$$32.52 - 31.86 = 0.66 \text{ cc.} = 0.70 \text{ per cent. free acid as sulphur trioxide.}$$

This result is in fair accord with the results obtained by the Beilstein and Grosset method of direct estimation, and probably corresponds closely to the amount of free acid actually present in the solid salt. It is entirely incorrect, however, to hold that the

solution of this alum will have that amount of free acid, as the results on p. 463 show that the amount of alumina in solution is slightly greater than the amount necessary to form the normal salt. The solid salt is evidently not uniform. When dissolved in water to dilute solution, these inequalities disappear quickly. In concentrated solution, as in the Beilstein and Grosset method or when the salt is dissolved in citrate, equilibrium is attained much more slowly, and a titration of such a solution soon after solution is complete gives approximately the conditions prevailing in the solid salt. If the solution is allowed to stand a sufficient length of time, equilibrium is finally reached as shown by experiments C 3 and C 5, on page 461.

#### SUMMARY.

If a solution of an alum to which has been added neutral potassium sodium tartrate (Rochelle salt) is titrated with barium hydroxide, the barium hydroxide used will correspond to the sulphuric acid combined with the alumina plus the free acid. The sulphuric acid combined with sodium or potassium is not estimated. If a duplicate solution of alum is evaporated to dryness, redissolved in neutral sodium citrate and titrated with barium hydroxide, a smaller quantity of barium hydroxide is required, and the difference between the amounts of barium hydroxide used in the two titrations is equivalent to one-third of the alumina. From these two titrations can be calculated the alumina and the sulphuric acid combined with it whether the alum be basic or acid, and if the alum is acid, the excess of acid over that necessary to form the normal sulphate. Commercial aluminum sulphate may, in its solid state, carry free acid, although in the solution such uncombined acid may disappear, combining with what had been basic portions of the solid salt. Such free acid may be estimated by dissolving the solid salt directly in citrate and titrating with barium hydroxide at once. This method gives results closely concordant with Beilstein and Grosset's method, but it does not show that the alum contains more acid than is sufficient to form with the alumina the normal salt.

When aluminum sulphate is titrated with barium hydroxide thus, in presence of neutral alkali tartrate or citrate, the precipitation of barium sulphate is retarded for a time, varying from a few minutes to several hours and when the precipitate does form it is in a very peculiar colloidal form which is undergoing further

investigation. Consideration of this subject and also of the action of salts of other metals than aluminum and salts of other acids than tartaric and citric, as well as the theoretical points involved are reserved for a following paper.

ANN ARBOR, MICH.,  
December, 1901.

## THE ANALYTICAL CONSTANTS OF NEATSFOOT, TALLOW AND HORSE OILS.

BY AUGUSTUS H. GILL AND ALLAN W. ROWE.  
Received February 3, 1902.

OF the commonly occurring oils, fewer data are to be found about these three than about any of the others; this work was undertaken to supply this need.

The various tests were applied as described in a book published by one of us;<sup>1</sup> that is, the specific gravity was taken with a correct Westphal balance at 15° C. or 100° C.; the Valenta test was done with an equal quantity of glacial acetic acid, proved to be 100 per cent. by titration; the Maumené test was performed with 100 per cent. sulphuric acid, its strength also determined by titration, in a jacketed beaker, the acid being run into the oil drop by drop from a burette; the iodine number, with the solutions after having been mixed twenty-four hours, and the oils allowed to stand for four hours with it. The titer test was carried out as prescribed by Lewkowitsch, the acid being melted in a 5" test-tube held in a 100 cc. round-bottomed flask. The results given are usually the average of two closely agreeing determinations. The oils used were obtained from different dealers and guaranteed pure.

The constants are as follows:

	Sp. gr. 15° C.	Valenta. ° C.	Maumené. ° C.	Sp. temp. reaction.	Iodine. No.	Titer test. ° C.	Iodine No fatty acid
Neatsfoot oil, 1.	0.915	70.0	42.2	87.9	72.9	19-20	68.6
" " 2.	0.914	75.5	42.2	87.9	72.9	18-19	64.6
" " 3.	0.919	51.0	49.5	103.1	67.1	17-18	67.3
" " 4.	0.916	61.5	42.2	87.9	72.1	16	69.5
" " 5.	0.916	75.5	42.2	87.9	66.0	25.5-26.5	63.6
Usual figures ...	0.915	....	48.0	....	70.0	26.0	....
	100° C.						
Tallow oil, 1....	0.794	73.5	35.0	72.9	55.8	35-36	54.6
" " 2....	0.794	71.0	35.0	72.9	56.6	36.5-37.5	57.0
" " 3....	0.794	75.7	35.0	72.9	56.7	34.5-35.5	56.6
	15° C.						
Usual figures ...	0.916	47.0	43.0	....	57.0	39	....

<sup>1</sup> Gill: "A Short Handbook of Oil Analysis."

Color, etc.	Sp. gr. at 15°C.	Valenta. °C.	Maumené. °C.	Sp. temp. reaction.	Iodine No.	Iodine No. of clear oil.	Titer test. °C.	Iodine No. of fatty acids.
{ White-brown semi fluid }	0.919	80.2	46.0	95.8	75.1	....	32.5-33.5	72.9
{ Dark brown semi liquid }	0.916	54.0	52.1	108.5	82.5	82.0	30.0-31.0	72.3
{ Yellow-brown liquid }	0.922	71.0	54.7	114.0	86.3	83.7	25.0-26.0	78.7
	100° C.							
{ Golden brown nearly solid }	0.798	48.0	54.2	112.9	79.9	81.8	30-31	80.4
Very like, 4	0.799	61.0	53.5	111.5	78.8	78.2	34-35	82.1

Neatsfoot oils : the samples are fairly concordant with the exception of No. 3 ; the gravity and Maumené test are higher than those of the others ; as no adulterant could be proved, it is supposed genuine.

Tallow oils : the results here, upon oils from different sources, are remarkably concordant.

Horse oils : as was expected from their different appearance, these show a considerable variation ; the Valenta test is of no use whatsoever here ; No. 5 came from a young horse ; nothing is known about the others.

Were either of these oils used to adulterate neatsfoot, the horse oil would raise the Maumené and iodine values, and the titer test ; tallow oil would lower the Maumené, and iodine values, and raise the titer test quite considerably.

## A TEST FOR THE GUMMING QUALITY OF LUBRICATING OILS.

BY AUGUSTUS H. GILL.

Received February 3, 1902.

SOME years ago in studying the Elaidin test for oils, a few of the mineral lubricating oils were included, and it was noticed that those which deposited the most "tar" apparently changed the most in use. The test, other than a repetition with different oils, lacked confirmation as to its value except in one case. It was noticed that with a 25° paraffin oil the outside of the can containing it—where it was exposed to the air in thin layers—was covered with a skin closely resembling that produced

by linseed oil. The object of this work was to show that there is a connection between the amount of change ("tar") and the quantity of oxygen absorbed. The gumming test was applied after the manner of the Elaïdin test by treating 5 grams of the oil in a cordial glass with 11 grams of Roth's liquid (nitrosulphuric acid) the two being thoroughly stirred together and cooled by immersion in a pan of water at 10°-15° C. Brownish spots or, in case of a bad oil, masses form around the edges and become red in the course of two hours. The nitrosulphuric acid is prepared by saturating sulphuric acid of 46° Bé., containing a few drops of nitric acid, at 0° with nitric oxide.

The quantity of oxygen absorbed was determined by sealing 5 to 10 grams of the oil in a flask and heating it to 80°-105°, the flask being occasionally shaken. The oil was weighed into the flask, care being taken that none touched the neck; the neck was drawn down to a long thin-walled capillary, the flask allowed to cool at 20°, and then quickly sealed in a small blast-lamp flame. After heating about 100 hours the flask was allowed to cool to 20°, the capillary broken under water and the inflowing water weighed. This represented the number of cubic centimeters of oxygen absorbed from the air. The results are shown in the table. It was thought that possibly a difference between these oils might be shown by either the bromine, iodine or Maumené tests: the differences were, however, so slight as to show that these could not be used as a means of distinguishing between the oils.

The results should be compared crosswise of the table, as the temperatures, time of exposure, and amount of shaking varied with each test. With the engine oils the amount of tar formed seems to bear a close relation to the quantity of oxygen absorbed; this does not apparently hold true of the spindle oil tested.

Name of oil.....	1. 25° par- affin.	2. Red lubri- cating.	3. No 1 en- gine.	4. No. 1 spindle.
Appearance in gum- ming test.....	Dark brown pitchy cake.	Some dark pitch.	Dark brown, trace of pitch.	Medium brown, no pitch.
Oxygen absorbed per 100 grams oil at 80°.....	cc. 45.6 46.0	cc. 60.0 62.3	cc. 12.2 13.0	cc. 36.0 41.5
Oxygen absorbed at 80°- 85°, 12 days.....	190.5 180.0 105.4 101.6	.... .... 121.0 ....	34.1 .... 35.6 36.4	159.5 160.9 54.6 50.4
Oxygen absorbed at 98°- 115°, 12 days.....	.... ....	427.0 402.0	111.0 104.0	321.0 320.0
Oxygen absorbed at 95°- 105°, 12 days.....	188.0 170.0	238.0 272.0	65.0 ....	251.0 ....

## ANALYSES REQUIRED FOR AN ELECTROLYTIC ALKALI WORKS.

BY J. H. JAMES AND J. C. RITCHEY.

Received February 15, 1902.

WHILE in the main the analytical methods for an electrolytic alkali works are the same as used in the old processes of caustic and bleach manufacture, we have found in practice that the modifications given below facilitate the operations required. Some of the analytical methods necessarily have to be varied from those of the old processes because of the inherent difference in the electrolytic method of manufacture.

The analyses given below, which are used for a plant working a mercury cathode process, may be discussed under the following heads: (1) Raw Materials; (2) Factory Control; (3) Finished Products.

### RAW MATERIALS.

#### *Limestone.*

Determinations: Silica, ferric oxide and alumina, calcium carbonate, magnesium carbonate. These determinations are carried out in the usual way. A limestone as high as possible in calcium carbonate is required.

#### *Slaked Lime.*

Determinations: Water and carbon dioxide.

*Water.*—The workmen in the lime house become so expert in the slaking that they can generally tell by the physical characteristics when just enough water has been added, hence a water determination is not often required. When a sample comes to the laboratory it is quartered down quickly to about one ounce, and one gram heated for one hour over a blast-lamp. The loss in weight is reported as total water.

*Carbon Dioxide.*—This is rarely determined and usually amounts only to one- or two-tenths of a per cent. The determination is made in the usual manner with a Schroetter or other apparatus used in the analysis of carbonates.

#### *Salt.*

Determinations: Insoluble in water, calcium sulphate ( $\text{CaSO}_4, 2\text{H}_2\text{O}$ ), calcium chloride ( $\text{CaCl}_2, 6\text{H}_2\text{O}$ ), magnesium sulphate ( $\text{MgSO}_4$ ), magnesium chloride ( $\text{MgCl}_2, 6\text{H}_2\text{O}$ ), sodium sulphate ( $\text{Na}_2\text{SO}_4$ ), ferric oxide and alumina, and sodium chloride.

We make the analysis on the sample which has been dried over night in the steam oven at 100° to 105° C., and calculate the above salts according to the laws for the distribution of acids and bases, the determinations being ferric oxide and alumina, lime, magnesia, sulphur trioxide, and chlorine. Since the ferric oxide and alumina are usually very small in amount, they are not regarded in the distribution of acids and bases, but reported as weighed.

A salt low in sulphates and lime salts is required, as these accumulate and foul the electrolyte.

*Water.*

Determinations: Total solids and complete analyses of inorganic constituents. These determinations are made in the usual manner. A water low in sulphates and lime salts is required for the same reason as above.

FACTORY CONTROL.

*Caustic Liquor.*

Determinations: Sodium hydroxide and sodium chloride. Five cc. of the liquor as it comes from the cell is taken, the alkalinity determined by normal sulphuric acid with phenolphthalein as indicator, then a few drops of neutral potassium chromate solution are added and the sodium chloride determined by decinormal silver nitrate.

In this way, individual cells tests are made once each day and a test on the average liquor from each unit of forty cells is made every two hours throughout the twenty-four.

*Spent Brine.*

Determinations: Specific gravity at 60° F., free chlorine, sodium hypochlorite, sodium chlorate, sodium chloride, sulphur trioxide, iron and aluminum oxides, lime, magnesia and mercury. About one liter of the brine is required for the tests. The results are reported in grams per liter.

*Specific Gravity.*—The specific gravity is best determined by cooling a portion of the brine to 60° F., and taking the reading with a Westphal or Mohr balance.

*Free Chlorine.*—Pipette out two portions of brine of 50 cc. each into 8-oz. Erlenmeyer flasks, add 10 cc. of a saturated solution of potassium iodide, shake well, stand five minutes, titrate the lib-



erated iodine with decinormal hyposulphite, using starch solution as indicator. Multiplying the number of cubic centimeters "hypo" solution required by  $0.00355 \times 20$  gives the number of grams of free chlorine per liter.

*Sodium Hypochlorite.*—Two portions of brine of 50 cc. each are pipetted into 200 cc. beakers and the free chlorine + sodium hypochlorite determined with decinormal arsenious acid (Penot's method), using drops of starch solution and potassium iodide on a spotting plate as indicator. Deduct from this the number of cubic centimeters of "hypo" required for the free chlorine, and multiply the remainder by  $0.003724 \times 20$ , which gives the number of grams of sodium hypochlorite per liter.

*Sodium Chlorate.*—For this determination we prefer the following modification of the method given in Sutton's "Volumetric Analysis."

Take either the solutions from the sodium hypochlorite titration or pipette out two portions of 50 cc. each into 8-oz. Erlenmeyer flasks, and run in the number of cubic centimeters decinormal arsenious acid solution as determined above. Weigh out a quantity of C. P. ammonium ferrous sulphate in excess of the chlorate (unless it is known about how the brine is running in chlorate, several trials may be required to find this weight). Add the ferrous salt to the solution in the Erlenmeyer flask, close the mouth of the flask with a small funnel and place on a hot plate or sand-bath. Add 15 cc. concentrated sulphuric acid through the funnel (about 1 cc. at a time) slowly, allow to come to a gentle boil and remain so for three or four minutes. Then cool the solution and titrate the excess of ferrous salt with potassium bichromate. Multiply the amount of ferrous iron present by 7 to obtain the weight of ammonium ferrous sulphate in excess. Deducting this from the amount weighed out gives the ferrous salt oxidized by the chlorate decomposition, and this multiplied by  $25.51 \times 0.001775 \times 20 =$  number of grams of sodium chlorate per liter, or the same result is obtained by multiplying the weight of iron oxidized by  $0.3169 \times 20$ .

*Sodium Chloride.*—Instead of making the titration for sodium chloride in the same solution in which the chlorates were determined, as recommended by Sutton, we find it quite as accurate and more rapid to proceed as follows: Take 50 cc. of the cooled solution just after reading the specific gravity, and dilute to 1

liter with distilled water. Pipette out portions of 10 cc. each and titrate with decinormal silver nitrate, using about 8 drops of a 10 per cent. solution of neutral potassium chromate as indicator. Multiply the reading in cubic centimeters by 100, deduct from this the number of cubic centimeters of arsenious acid solution required in the free chlorine + sodium hypochlorite titration, which is a sufficiently accurate correction for the free chlorine and sodium hypochlorite present; the remainder multiplied by  $0.00585 \times 20$  gives the number of grams of sodium chloride per liter.

*Sulphur Trioxide.*—Pipette out 2 portions of 50 cc. each, add to each 50 cc. water with 3 cc. concentrated hydrochloric acid, and boil violently to completely decompose all hypochlorites and chlorates. When the smell of chlorine has disappeared, add slowly to the boiling solution 10 cc. of saturated barium chloride solution which have been diluted to 50 cc. and heated to boiling. Allow to stand until the precipitate settles, filter, wash with hot water to free precipitate from chlorides, dry, ignite, and weigh barium sulphate, and from this, calculate the sulphur trioxide.

*Ferric Oxide and Alumina, Lime, and Magnesia.*—Two portions of 100 cc. each are pipetted out, 50 cc. water with 3 cc. concentrated hydrochloric acid added to each, and the solutions then boiled violently until the smell of chlorine has disappeared. The precipitation and weighing of ferric oxide and alumina, the determination of the lime, and the precipitation and weighing of the magnesia are conducted the same as in an ordinary limestone analysis.

*Mercury.*—Two portions of 50 cc. each are pipetted out, 50 cc. of water with 3 cc. concentrated hydrochloric acid added to each, and the solutions boiled violently for several minutes. When the smell of chlorine has disappeared, pass hydrogen sulphide through the hot solution until the mercury is all precipitated. Filter on a Gooch filter that has been previously dried at  $100^{\circ}\text{C}$ . for one hour and weighed. Wash the precipitated mercuric sulphide with hydrogen sulphide water until all the sodium chloride is removed, then with alcohol, next with ether, then with carbon bisulphide until all the free sulphur is removed. Finally wash out the carbon bisulphide with ether, then follow with alcohol, dry at  $100^{\circ}\text{C}$ . for one hour and weigh as mercuric sulphide. Calculate to mercury and report as such.

A complete analysis of the spent brine as above is made each week on a sample which represents an average of all the cells. Individual cell tests on the brine for sodium chloride alone are made once per day. A complete brine analysis with the exception of the magnesia can be made by one chemist in about four hours. The magnesia, precipitated as ammonium magnesium phosphate, is allowed to stand over night and finished the next morning.

#### *Chlorine Gas.*

Determinations: Chlorine and hydrogen.

These tests are made with an ordinary Orsat-Muencke gas analysis apparatus, having two pipettes filled with a solution of potassium iodide and caustic potash which serve for the chlorine absorption (the small amount of carbon dioxide gas present is negligible), while a palladium tube is attached for absorbing the hydrogen.

These tests are made on the gas once each day.

#### FINISHED PRODUCTS.

##### *Caustic Soda.*

Determinations: Sodium hydroxide + sodium carbonate, and sodium chloride (other determinations to make a complete analysis are rarely asked for).

The sample, which usually comes to the laboratory still hot, should be taken from the bottle, piece by piece, and broken quickly in a mortar to pieces no larger than a pea, bottling again as quickly as possible. When all is broken, mix sample thoroughly by turning the bottle over and over. The bottle should not be more than two-thirds full to insure a thorough mixing. Take a weighing bottle, which has been previously dried and weighed, and fill it with caustic from the mixing-bottle, close bottle, and reweigh. Empty the caustic from the weighing-bottle into a beaker, dissolve and pour caustic solutions and rinsings into a liter flask. Dilute nearly to the mark, cool under the tap to a temperature approximately that of the room, dilute to the mark, mix thoroughly by turning the stoppered flask end over end.

*Sodium Hydroxide + Sodium Carbonate (Total  $\text{Na}_2\text{O}$ ).*—Pipette out 50 cc. of the caustic solution into a beaker, add 4 or 5 drops of methyl orange indicator and titrate with normal sulphuric acid.

Repeat the titration on 50 cc. portions until a constant reading is obtained. Multiply the number of cubic centimeters used by  $0.031 \times 20$  and divide by the weight of caustic taken; this gives the per cent. of total  $\text{Na}_2\text{O}$  in the sample, *i. e.*, the  $\text{Na}_2\text{O}$  existing as carbonate and hydroxide, the small amount existing as sulphide and sulphite, etc., being disregarded.

*Sodium Chloride.*—Pipette out two cc. portions of the caustic solutions into beakers of 250 cc. capacity, carefully neutralize with nitric acid, and titrate the sodium chloride with decinormal silver nitrate as usual.

The caustic soda analysis is usually limited to a determination of the total  $\text{Na}_2\text{O}$ , which is made on a sample from each pot as it is finished.

#### *Bleaching-Powder.*

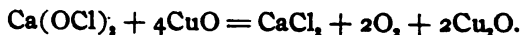
Determinations: Available chlorine, water, carbon dioxide, total chlorine.

*Available Chlorine.*—This test is best made by the old arsenious acid titration (Penot's method).

*Water.*—We have been unable to find a perfectly satisfactory method for this determination, but have used the following:

One gram of the bleaching-powder is quickly mixed with about 5 grams of dry copper oxide and placed in a porcelain boat near the back part of a 12-inch combustion tube. Beyond the boat the tube is filled with scrap sheet silver mixed with cement silver which should be in a spongy condition. A weighed Geissler bulb containing sulphuric acid is attached for absorption of the water. Two similar bulbs are attached at the other end for drying the air which enters the tube. The tube is heated gently at first, dry air being aspirated slowly through the apparatus, finally the heat is raised immediately under the boat as high as the tube will stand and kept so for an hour and a half. The sulphuric acid bulb is detached and weighed in the usual manner.

This method of retaining the chlorine is based on the following reaction:<sup>1</sup>



The silver serves to retain any chlorine that may escape from the boat.

*Carbon Dioxide.*—For this determination a train was arranged

<sup>1</sup> Richter's "Inorganic Chemistry," p. 370.

as follows: First, two potash bulbs for removing the carbon dioxide from the air entering the apparatus; second, a flask of about 100 cc. capacity fitted with a stop-cock funnel for introducing the acid for decomposition; third, three Geissler bulbs filled with a nearly saturated potassium iodide solution for absorption of the evolved chlorine; fourth, a U-tube containing fused calcium chloride lumps free from caustic for absorption of water from the gas before it enters the potash bulb; fifth, a weighed potash bulb for the absorption of the carbon dioxide.

One gram of the bleaching-powder is placed into the decomposition flask and about 15 cc. of dilute hydrochloric acid (1:4) dropped in from the stop-cock funnel, a current of air being slowly aspirated through the apparatus. The chlorine is all absorbed in the first and second potassium iodide bulbs, the third remaining colorless. To remove the carbon dioxide that is absorbed by the potassium iodide solution, the aspiration of the air is continued for two hours after the bleaching-powder is decomposed. While there is a possibility of iodine vapor being carried over into the potash bulb, we have had no such trouble as the third potassium iodide bulb, remains colorless throughout the operation. The potash bulb is detached and weighed in the usual manner.

*Total Chlorine.*—One-half gram of the bleaching-powder is reduced with arsenious acid solution as in the available chlorine test, then neutralized with nitric acid and the chlorine determined in an aliquot part with decinormal silver nitrate solution; this gives the chlorine existing as hypochlorite and chloride. A determination of the chlorates present by the method under spent brine analysis, is made on one-half gram of the sample. It is better, however, to use hydrochloric acid for the chlorate decomposition here. For these results the total chlorine is calculated.

Of the above determinations, the available chlorine is the only one made in daily practice. This analysis is made on the chamber that is "up to strength" just before the charge is withdrawn for packing.

Nearly all the above analyses are made at this laboratory for Mr. B. E. F. Rhodin, managing director of the Canadian Electro-Chemical Co., to whom we are indebted for many suggestions and courtesies.

## BURETTE ARRANGEMENT.

BY E. M. JOHNSON.

Received February 15, 1902.

THE burette arrangement here shown has been found very satisfactory and convenient in a metallurgical laboratory where a number of standard solutions are in use every day. The glass tube *B* is connected direct to the three-way burette by a short rubber tube *A*. This connection should be made so as to bring the ends of the glass tubes very near to each other, practically doing away with any contact between the standard solution and the rubber. There is no pressure on the rubber connection, consequently no leakage, as is the case when the burettes are filled by force of gravity. The burette is held in place by an ordinary bird cage spring *C*, and can be easily detached and cleaned by disconnecting the connection *A* and unhooking the spring. It is easier to replace an empty standard solution bottle than is the case with other devices. This is done by simply disconnecting at *A* and running the glass tube *B* up high enough to put in a full bottle. The glass tube *B* should slide with ease through the rubber stopper. The surface of the glass plate next to the table may be painted white, or some suitable white material placed under it. It is very easy to keep the glass plate clean.

DENVER, COLORADO,  
February 12, 1902.

---

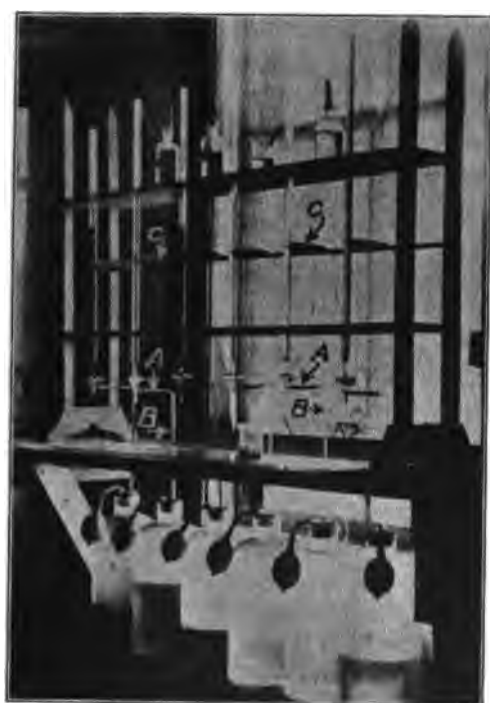
## A GENERATOR FOR HYDROGEN SULPHIDE.

BY J. N. SWAN.

Received January 20, 1902.

OF the making of apparatus for the generation of hydrogen sulphide there is no end. One would think that out of the more than 200 acetylene generators on the market a machine might be chosen which would at least approximate perfection as a generator for hydrogen sulphide. If one generates the gas on the large scale and uses a gasometer with pipes leading to the places where the gas is to be used there are machines which give satisfactory results. If, however, it is desired to use the gas in fairly small quantities as, *e. g.*, with an ordinary class in qualitative analysis, there is still something to be desired in the way of a machine that will give satisfactory results in every particular.

The machine herewith illustrated has been used for such work



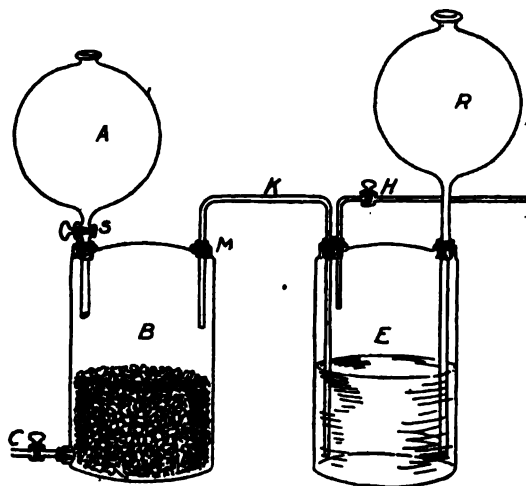




in this laboratory with better results than had been obtained before, using a number of different forms of generators. The generator was made by assembling ordinary laboratory apparatus.

Referring to the figure, a two-necked Woulfe flask, *B*, contains the iron sulphide. Into one neck is fitted a separatory funnel, *A*, with a stop-cock, *S*. This funnel contains the dilute acid. *E* is a second two-necked Woulfe flask. Into one of the necks of this flask a tube, *R*, is fitted so that it reaches nearly to the bottom of the flask. The upper part of this tube contains a large bulb. The inner part of a Kipp apparatus is a good tube for the purpose. A tube, *K*, connects the two flasks and terminates under the water with which *E* is partly filled. An exit tube, *H*, with a stop-cock, forms the tube which delivers the gas ready for use.

To generate the gas, the stop-cock *S* is turned and a small quantity of the dilute acid is allowed to trickle down upon the sulphide in the Woulfe flask. As the gas is generated it passes through *K* into the flask *E*, in which passage it is washed by



bubbling up through the water in *E*. At the same time the pressure of the gas collecting in *E* will force the water up into *R*. By turning the stop-cock *H*, a supply of gas is received under the pressure of the head of water in *R*. If an excess of acid is permitted to flow out of the separatory funnel the gas generated by it will be stored in *E* ready for the next time it is to be used.

The spent acid can be removed at *C* at any time, and the flask

*B* thoroughly washed out by disconnecting at *M*, and allowing a stream of water to flow through the flask. This can be done without disturbing the acid in *A*. When fresh water is put into *E*, sufficient gas to saturate the water should be passed into it slowly if the machine is to stand for any length of time before being used. This will prevent the water from running back into *B* on standing.

It is probable that the chief advantage in this form of machine is that there are no narrow tubes to become clogged with salts crystallizing from the spent acid. In actual practice it has been found that there is a minimum amount of gas wasted and a maximum amount of time saved in caring for the machine as compared with other machines in common use.

MONMOUTH, ILLINOIS.

## THE DETERMINATION OF COPPER BY ALUMINUM FOIL.

By GEORGE E. PERKINS.

Received February 7, 1902.

THE following method is a modification of the process by A. H. Low. The copper is brought into solution as a sulphate by treatment similar to that in Low's modified cyanide process. The solution is evaporated until all nitric acid has been driven off and dense white fumes appear. Water is added until the dilution is about 50 cc. of water to 10 cc. of sulphuric acid. Sheet aluminum of about 25 gauge thickness is cut into pieces about 40 mm. square with one corner of each piece turned up for convenience in handling. Two or three of these pieces are added to the beaker containing the solution of copper. The solution is then boiled. In about five minutes, all of the copper is precipitated upon the aluminum sheets.

Instead of redissolving the deposited copper and titrating with cyanide solution, more satisfactory results are obtained by washing the deposited copper into a tared Gooch crucible, by giving a final wash with alcohol and by burning off the alcohol and drying. Weigh the result as metallic copper.

In forming the filter, care should be taken that only sufficient asbestos fiber is used to produce a good filter. In washing with alcohol and burning, the same care is needed as in the electrolytic method that too much alcohol is not used.

PROVIDENCE, R. I.,  
February 3, 1902.

<sup>1</sup> Read before the January meeting of the Rhode Island Section of the American Chemical Society.

# SUPPLEMENTARY NOTE TO A "GRAVIMETRIC METHOD FOR THE ESTIMATION OF HYDROGEN DIOXIDE."

BY GEORGE E. HOSCH.

Received February 28, 1900.

IN This Journal, 23, 923, the author describes a method for determining the strength of hydrogen dioxide by the use of a "Schrötter" alkalimeter. Upon further experiment, he finds that a Geissler style modified by Dr. Shepard with removable parts, is a more convenient form, especially where a number of assays are to be made in succession. When the decomposition is complete, and if the apparatus is aspirated for about three minutes with air which had been previously dried by calcium chloride, the results obtained are much more satisfactory. A saturated filtered solution of bleaching-powder may be substituted for the potassium permanganate, as already suggested, but instead of dilute sulphuric acid a weak solution of caustic soda must be used in the bulb, and as in the case of permanganate, divide the results obtained by 2. But the most consistent results may be obtained by employing a filtered saturated solution of lead acetate as a decomposing substance for the hydrogen dioxide. As this is a catalytic action (all the oxygen generated comes from hydrogen dioxide itself), one may operate upon as much as 5 cc. of the hydrogen dioxide, but this precaution must be observed; in working with commercial samples or those which contain much free acid, a weak solution of caustic soda should be used in the bulb, as in the case of the bleaching-powder. The following tables are the results (in per cent.) obtained from pure and commercial samples of hydrogen dioxide, employing the different decomposing substances, just mentioned:

## MEDICINAL SAMPLE, 0.05 PER CENT. FREE ACID (HCl).

$\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$ .	$\text{Ca}(\text{ClO})\text{Cl}$ .	$\text{KMnO}_4$ .	$\text{KMnO}_4$ volumetric.
3.01	2.95	3.30	....
2.98	2.99	2.86	....
2.99	3.00	3.11	....
Average, 2.99	2.98	3.09	3.01

## COMMERCIAL SAMPLE, 0.91 PER CENT. FREE ACID ( $\text{H}_2\text{SO}_4$ ).

$\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$ .	$\text{Ca}(\text{ClO})\text{Cl}$ .	$\text{KMnO}_4$ .	$\text{KMnO}_4$ volumetric.
1.01	0.93	1.07	....
1.05	1.03	1.09	....
Average, 1.03	0.98	1.08	1.05

## NEW BOOKS.

**ELEMENTARY ELECTRICITY AND MAGNETISM.** By DUGALD C. JACKSON, E.E., Prof. of Electrical Engineering, University of Wisconsin, and J. P. JACKSON, M.E., Prof. Electrical Engineering, Penna. State College. The Macmillan Company.

This volume will be appreciated by all persons who wish to acquire some knowledge of the subjects it presents. While the authors have written in an elementary way, every topic is as scientifically and exhaustively discussed as one would expect from an expert. In these days when electricity is applied so extensively, and when many employ it without adequate previous training as to its origin, its control, measurement, etc., the present volume comes as a reliable and trusty handbook. To chemists, who have not enjoyed a full training in physics, it cannot fail to recommend itself. It is well written and well illustrated.

EDGAR F. SMITH.

**ENZYMES AND THEIR APPLICATION.** By DR. JEAN EFFRONT, translated by S. C. PRESCOTT. Published by John Wiley & Sons, New York.

The interest in enzymes is growing very rapidly. The sphere of their application is largely increased both in theoretical and industrial chemistry. Biology is probably the science that has profited most from the study of enzymes, and many problems that were in darkness for decades lose their mysteriousness in the light of the new discoveries of certain functions of enzymes.

But the results of all the new investigations were never summed up in a systematic, brief and popular form. Prof. Effront's book supplied that gap in the chemical literature, and Mr. Prescott's translation of the work under the title "Enzymes and their Application" will be welcomed by all interested in the subject.

The present volume deals chiefly with the enzymes of the carbohydrates, and briefly with the oxidases. In the following volume the proteolytic enzymes and toxins will be discussed.

The book being a summary of a course of lectures delivered at the Institute of Fermentation at the University of Brussels, it naturally has a more or less elementary character, and cannot be regarded as a reference or text-book. But all the greater is its value for one who seeks a general knowledge on the subject both from theoretical and practical standpoints. The theoretical problems are discussed in a very clear and comprehensive way. The

introductory chapter on the synthetic and analytic work of the living cell is perhaps a little too brief, but the question of the "Manner of Action of Diastase" is discussed exhaustively in the light of the recent researches in organic chemistry. The author criticises the theory that enzymes are not a substance but a property, and adduces all the evidence for the theory of the chemical nature of the action of enzymes.

The question of the individuality of enzymes the author answers in the affirmative.

The mode of preparation of the different individual enzymes, and the favorable and unfavorable condition for their action is discussed in considerable detail, and sufficient room is given to the theoretical explanation of the experimental and practical findings. It seems, however, that the reversibility of the action of ferments is omitted in all the theoretical considerations of the author, and yet they could explain a good many facts for the explanation of which the author resorts to much more complicated views.

The chapters on industrial application of the enzymes read as interestingly as the theoretical discussions, and the book will undoubtedly be an inspiration to a good many workers in the line of biological chemistry.

The fact that the author verified most of the experimental data of other investigators mentioned in the book makes the book all the more valuable.

Mr. Prescott deserves much credit for the good translation of the book.

P. A. LEVENE.

REPRINTS OF SCIENCE CLASSICS NO. 1. THE ANALYSIS OF AIR AND WATER, being selections from LAVOISIER'S ELEMENTARY TREATISE OF CHEMISTRY. Translated and annotated by C. E. LINEBARGER. 1902. Ravenswood, Chicago, Ill. The School Science Press. Double number, pp. 31. Price, 10 cents.

The purpose of the little pamphlet before us is to place in the hands of pupils of high schools and colleges the exceedingly beautiful and clear account which Lavoisier gives of those experiments which first laid a secure foundation for our present knowledge of air and water. Dr. Linebarger's idea is a most happy one. It is difficult to think of anything better than this little booklet for riveting the attention and awakening the interest of beginners in scientific study. It is well worthy of perusal by older chemists

as well, for we all have much to learn from the great master of our science. W. A. N.

**STUDIEN ZUR KENTNISS DER ABHÄNGIGKEIT DER VISCOSITÄT DER FLÜSSIGEN KÖRPER VON DER TEMPERATURE UND VON IHRER CHEMISCHEN CONSTITUTION.** By Alexius Batschinski. 101 pp. 17 × 25 cm. Moscow. 1901.

Though large enough to be a monograph, this is really a reprint of a journal article. The author has previously called attention to the fact that with most liquids the product of the internal friction into the absolute temperature is a constant. Data are given showing the application of this law to one hundred and forty-four different substances. In general, the agreement is good ; but anhydrides, acids, alcohols and water form exceptions. These are all substances which we consider as polymerized in the liquid state.

WILDER D. BANCROFT.

**THE EXPERIMENTAL STUDY OF GASES.** By MORRIS W. TRAVERS, D.Sc. New York : The Macmillan Co.

Dr. Travers' book confines itself to methods of experiment which have been useful in researches on the properties of gases and to a description of some of the more important of such researches. It does not contain lecture experiments, nor instruction for beginners. In the selection of topics, it is well balanced, and as complete as can fairly be demanded of its 320 pages ; chapters on mercury pumps, on stop-cocks and other connections, on the collection and storage of gases, on reading instruments, and on calibration, have their due place. The chapters on the preparation of pure gases, on gas analysis, and on the determination of densities, are interesting and satisfactory, as are those on the relation of temperature, pressure, and volume, on vapor pressure and critical constants, and on specific heat.

The most interesting chapters, naturally, are those which have more or less to do with the newly discovered gases. That entitled "The Gases of the Helium Group" describes the method used in isolating argon, and that afterwards used to obtain it in considerable quantity, and narrates the steps which led to the discovery of helium, neon, krypton, and xenon. A chapter on the liquefaction of gases explains all the new principles which have been utilized and the new processes which have been used in liquefying gases since the time of the experiments of Pictet and of Cailletet. Here is found a clear account of Hampson's machine for liquefying air ; it is stated that this machine will

begin to deliver liquid air in four minutes from the time of starting it. A method is fully described by which liquid hydrogen may be obtained without great difficulty. A chapter entitled "The Manipulation of Liquefied Gases" will be thought by many to be the most interesting in the book. It treats of the separation of gases in a mixture by fractional distillation. One such separation was that by which, from a hundred liters of atmospheric nitrogen, there was obtained a residue containing ten per cent. of neon and helium; in the air, there is but one or two parts of neon in a hundred thousand, and perhaps a tenth as much helium. Another such separation is that of fifteen liters of argon; diagrams make clear the course of the experiment, by which, after two final distillations at the temperature of liquid hydrogen, neon was obtained in quantity sufficient for the determination of its density. A third such fractional distillation was that applied to liquid air, by which krypton and xenon were obtained; the course of this experiment is also made clear by the aid of diagrams. A proper end of this subject is made by the chapter on spectrum analysis, which contains convenient tables, as well as a map, of the spectra of the new gases.

The reading of proofs was careful; no misprints have been noted more serious than Hildebrand twice for Hillebrand, and Gimingham for Gimingham. Errors of fact are few and unimportant. Names of journals not published in England are cited somewhat carelessly; the Smithsonian Contributions to Knowledge appear as Proceedings of the Smithsonian Association, and the *Annales de Chimie et de Physique* is referred to in five different ways.

Dr. Travers' connection with the first workers on the new gases was so intimate, and his own part in some of the work was such, that he is especially well fitted to write this volume, which is a very welcome addition to scientific literature.

EDWARD W. MORLEY.

THE MANUFACTURE OF PAINT. BY J. CRUICKSHANK SMITH. London: Scott, Greenwood & Co. 1901. 200 pp. Price, \$3.00 net.

This author seems to know very well the kinds of machinery in use in England for making the cheaper grades of paint, and the illustrations are intelligently chosen and well executed. It is difficult for an American paint manufacturer to believe that modern high-class paint machinery has not yet found its way

into English factories, but very likely it is true. The only American machine described is one of the earlier forms of water-cooled mills; and the practical, technical points which one would like to find in a book of this sort, such as the values of different styles of dressing millstones for various kinds of work, the points of excellence to be aimed at in making particular paints, the nature and effect of the vehicles used, and the like,—such things as these are very scantily touched upon. It seems remarkable that no mention is made of the practice of mixing oil with wet white lead without preliminary drying, a practice of great commercial importance. In general, the information conveyed to the reader seems to be of the sort obtainable from the makers of paint machinery, rather than from experts in paint manufacture; accurate and useful as far it goes, but lacking in real knowledge of the subject. The book is one which should be of interest and use to the beginner but is not complete enough to serve the advanced manufacturer.

A. H. SABIN.

LEÇONS SUR LA THEORIE DES GAZ. L. BOLTZMANN; traduites par A. GALLOTTI. Paris: Gauthier-Villiers. 1902. Price, 8 francs.

Boltzmann is one of the three great mathematicians to whom the development of the kinetic theory of gases is mainly due. The present volume contains a translation of the first half of his lectures, originally published in 1896 and 1898, and gives a systematic account of the mathematical results attained by the joint labors of Maxwell, Clausius and Boltzmann.

Professor Gallotti's translation is clear and accurate; some sentences are even more perspicuous than in the original. Professor Brillouin has furnished an historical introduction and some comments on certain steps in the mathematical discussions of the author.

EDWARD W. MORLEY.

THE MANUFACTURE OF MINERAL AND LAKE PIGMENTS. BY DR. JOSEF BERSCH. TRANSLATED BY A. C. WRIGHT. London: Scott, Greenwood & Co. 1901. 476 pp. Price, \$5.00 net.

This admirable book was evidently written by a thorough chemist who is also a practical color-maker. Not many technical points escape mention and the book is valuable not only for reference but for daily use. The chapters on "Black Pigments," "Vermilion," and "Ultramarine," are especially valuable, as presenting an intelligible account of processes on which very little practical information is available.



It is, of course, impossible to write a book which nobody can find fault with; for example, our author gives barium chromate as a pigment under the name of "Permanent Yellow," and omits any mention of strontium chromate; the former is a very inferior color, not known in this country, while the latter, known under the same name and also as "Perfect Yellow," is one of the most beautiful pigments known and, in spite of its low opacity, is considerably used. Also in the chapters devoted to "Metallic Pigments" and "Bronze Pigments," no mention is made of metallic aluminum, one of the most valuable and widely used pigments in this class.

The part of the book devoted to "Lakes" is, in the judgment of the reviewer, hardly up to the standard of the rest of the book, not because of what it contains but what it leaves out. The author seems to have felt less interest in this subject and has treated it less in detail, but it seems to be correct as far as it goes. The book, as a whole, is very satisfactory.

A. H. SABIN.

THE ELEMENTS OF PHYSICAL CHEMISTRY. Second Edition. By J. Livingston R. Morgan. New York: John Wiley and Sons. 1902. 13 x 19 cm. x + 352 pp. Cloth. Price, \$2.00.

This book does not differ essentially from the first edition, which appeared in 1898, so that it would be superfluous to give an outline of its contents. The author states that he has endeavored, (1) to bring the subject matter up to date, (2) to make, wherever possible, the relations clearer than before, and (3) to make the book more useful to those studying the subject without an instructor. The changes made consist of a number of minor omissions and additions; a transposition of the chapter on the rôle of the ions in analytical chemistry, so as to form a part of the chapter on chemical change; and the addition of a final chapter containing problems for drill work.

The author has exerted himself to correct the numerous mistakes contained in the first edition; and yet, the new edition is by no means free from errors. It is impossible to cite all of these in detail here, but a few must be given by way of illustration. Thus on page 70 is the statement, "The surface-tension  $\alpha$  of a liquid is the force in grams, dynes (or milligrams) which is necessary to form a surface one centimeter (millimeter) in length." The theory ascribed to Brühl on page 268 is simply the Nernst-

Thomson view of the relation between the dielectric constant of a solvent and its so-called dissociating power. The new idea that Brühl does put forth in the article cited, is that dissociating power is due to the unsaturated condition (*i. e.*, to spare valences) of solvents. On page 269 we read, "Because substances dissolve and go into the ionic state with a loss of heat energy, does not show that there is a loss of energy to the system, but only that by the transformation heat energy as well as electrical energy are given up."

The italicised statement on page 93 that "the osmotic pressure depends upon the solute and is independent of the nature of the solvent," and that on page 100, "those substances, and only those, which give abnormal osmotic pressures in solution are capable of conducting the electric current, and if they are dissolved in other solvents in which they behave normally, they lose this power", can no longer be considered "up to date."

A brief treatise on general physical chemistry which devotes such an undue proportion of its space to the exposition of the theory of electrolytic dissociation and its applications (without even attempting to indicate the shortcomings of this hypothesis) as this book does, can at the present stage of the development of the science, hardly claim to present the subject in a fair, well-balanced form.

LOUIS KAHLENBERG.

OUTLINES OF ELECTROCHEMISTRY. BY HARRY C. JONES. New York: The Electrical Review Publishing Co. D. Van Nostrand Company. 1901. vi + 106 pp. Price, \$1.50.

Contributed originally to the pages of the *Electrical Review*, the articles forming the chapters of this book are designed for the information of those interested in or concerned with electrical engineering, as well as for the student of the subject from the purely scientific standpoint. The author disclaims any pretensions to their forming a systematic treatise, yet the subject is treated in such a manner as to introduce the reader by comparatively easy steps to a knowledge of osmotic pressure and the ionization theory of solution, and of the bearings of these matters upon electrochemistry. The later chapters deal particularly with the calculation of the electromotive force of galvanic elements. While it may be admitted that, upon the whole, the book conveys to the so-far initiated reader a clear idea of the subject, and that a number of the chapters leave little to be desired as semi-

popular articles, there are parts which can scarcely be regarded as quite satisfactory. On page 40, for instance, under the heading of "The Present Theory of Electrolysis," sufficient evidence is not furnished to carry conviction regarding the assertion that "we must abandon the theory of electrolysis which involves the secondary decomposition of water." When there are two different kinds of anions around the anode in electrolysis—in the case of hydrochloric acid, for example, chlorine ions from the ionized acid and hydroxyl ions from the ionized water—is it quite obvious, as the author asserts, that the ions which will give up their charges to the anode are the ones which hold them less firmly? Has the effect of the varying proportions in which the two kinds of ions may be present not been overlooked here? The author's statements seem convincing enough where only exceedingly low current densities are in question; but is it justifiable to make the unqualified assertion that "the anions move to the anode, but do not give up their charges; the hydroxyl anions from the water give up their charges instead?" (page 42). How is the formation of persulphuric acid at the anode to be explained on such an assumption? It is true that a few pages further on the effect of increased current density is referred to, but in such a way that the uninformed reader is very likely to overlook its importance.

A rather misleading description of the porous earthenware vessel used as a support for the semipermeable membranes employed in making osmotic pressure determinations, is given on pages 6 and 7, where it is referred to as "porcelain," whereas true porcelain is really non-porous.

The rather inconvenient shape of the book is, no doubt, due to the type having been set up originally in column form for the review in which the articles appeared. The matter should have undergone more careful revision before being issued in book form, as a number of mistakes have escaped correction. Vagaries of linotype setting are obviously responsible for the omissions and dislocations, on page 63, column 2, lines 5 and 6, and on page 83, column 2, line ten from foot. Humphrey Davy and Borchers appear instead of Humphry Davy and Borchers respectively (pages 2, 32, 43). A figure should have been prepared for page 83, to conform with the description in the text. It can scarcely be doubted that Walker would object to being represented as the author of the general electrolytic method, mentioned on page 45,

of passing from one dibasic acid to another richer in carbon atoms.

In conclusion, the following pronouncement of the author may be warmly commended: "In a word, the proper place to lay the foundation for the career of the practical man is in the University."

LEONARD DOBBIN.

**DRYING OILS, BOILED OIL, AND SOLID AND LIQUID DRYERS.** BY **LOUIS EDGAR ANDÉS.** London: Scott, Greenwood & Co. 1901. 342 pp. Price, \$5.00 net.

In times past this author has been a serious offender in the way of writing books which were merely compilations of what other people had said or guessed, so that we look with suspicion on a new book from him; but in this instance we are agreeably disappointed. Mr. Andés evidently knows something about drying oils, and has a lot of practical experience in their treatment and use. It is the best book on the subject and is pretty well up to date. The book indeed contains many of the old, useless, and impracticable formulae, familiar to all students of the subject, but these are compensated by remarks from the author's own experience which are fairly luminous with good sense and accurate knowledge, such as characterize the chapter on "Dryers." To get the real value of the book one must differentiate between the things which the author knows and those which he has merely read about; but to one reasonably familiar with the subject, this is not difficult, and to such the book will be found very useful. It is worth buying.

A. H. SABIN.

VOL. XXIV.

[ JUNE, 1902. ]

No. 6.

# THE JOURNAL

OF THE

# AMERICAN CHEMICAL SOCIETY.

---

[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY,  
No. 61.]

## THE ATOMIC WEIGHT OF ARSENIC.

BY W. CLARENCE EBAUGH.<sup>1</sup>

Received February 19, 1902.

### INTRODUCTION.

IN the present state of our knowledge concerning the relative atomic weights of the elements, any additional evidence in regard to the generally accepted values will be welcomed. It is not enough to repeat old methods of determination and to follow out old lines of comparison. What is needed is the introduction of new analytical methods, new comparisons, and new ratios. In this way we can reenforce results obtained by earlier investigators or discover in them the existence of errors due to faulty methods of analysis or to impurities in the substances used in such investigations. It was with this guiding thought that the present redetermination of the atomic weight of arsenic was undertaken, and the result should be looked upon as a contribution to our knowledge of this constant. In no sense can it be regarded as conclusive, although in many respects it is certainly confirmatory.

<sup>1</sup> From author's thesis for Ph.D. degree, University of Pennsylvania, 1901.

In an earlier study of the atomic weight of arsenic, Hibbs<sup>1</sup> applied a method that has frequently been used with success in other determinations; *viz.*, the conversion of sodium pyroarsenate into sodium chloride in a current of hydrogen chloride gas. Thus a new ratio (NaCl:As) as well as a new factor (Na) was introduced into the calculations. It seemed desirable to extend this method to other arsenic-containing substances; therefore silver arsenate, lead arsenate, barium arsenate, magnesium pyroarsenate, sodium sulpharsenate and sodium cacodylate were prepared with the intention of converting them into the halogen salts of their respective metals. If practicable these halides were to be reduced to metal by heating them in a current of hydrogen. Thus we would have the ratios



where Me represents silver, lead, barium, magnesium and sodium, and Hal represents chlorine, bromine and iodine. As additional factors there would be introduced oxygen, sulphur, carbon and hydrogen.

Much of the work was disappointing, but it is believed that the data gathered from the experiments, when the preconceived ideas were capable of execution, will be of value as a contribution to our knowledge concerning the atomic weight of arsenic.

#### HISTORICAL.

The atomic weight of arsenic has been studied by six investigators. Seven methods of attacking the problem were used.

It is astonishing how closely the result of Berzelius' single experiment (75.02) accords with the means of the series of experiments which followed. Dumas' first value (74.985) is also remarkable in view of the complicated method of investigation employed by him. Kessler, in a paper published in 1861, seems to throw doubt upon his own results (75.175), since he finds that they are influenced by (a) the time of contact of his solutions with the air, and (b) the dilution of the solutions used. Why Wallace should have obtained results more than 0.8 of a unit (74.229) lower than his predecessors, is inexplicable.

The generalizations of Van der Plaats, Ostwald, Seubert, Rich-

<sup>1</sup> Hibbs: Thesis, University of Pennsylvania, 1896.

ards, and Clarke, agree in assigning to arsenic the atomic weight 75, plus or minus a small probable error.

#### PREPARATION OF MATERIAL.

*Silver Arsenate.*—Silver nitrate was prepared from silver that had been subjected to the well-known purification method of Stas. Arsenious oxide was sublimed in an apparatus like that employed by Gattermann<sup>1</sup> in making aluminum chloride. The sublimed product was converted into arsenic acid by E. Kopp's method; i. e., boiling 4 parts of arsenious oxide with 12 parts of nitric acid (sp. gr. 1.20) and 1 part of hydrochloric acid (sp. gr. 1.20). The arsenic acid was boiled down twice with an excess of nitric acid and then diluted to a definite volume. Ammonia water (sp. gr. 0.90) was boiled gently in a large flask, and the evolved ammonia led through an empty flask (which served as a condenser) into distilled water. The purified ammonium hydroxide and arsenic acid were then united in the proportions required to make triammonium arsenate. This solution was dropped gradually into a solution of silver nitrate; the precipitated silver arsenate was filtered out, washed thoroughly and dried at 150°-170° C.

*Lead arsenate.*—Disodium hydrogen arsenate (Merck) was recrystallized several times, dissolved in water and allowed to stand for some hours. Pure lead acetate of commerce was likewise subjected to three recrystallizations, dissolved in water and allowed to stand. The solution of lead acetate, filtered into a large beaker, was well diluted and treated with the filtered solution of disodium hydrogen arsenate. Constant agitation was maintained during the precipitation. The lead arsenate was allowed to subside and then washed by decantation until all soluble lead and alkali salts were removed. Drying at 150°-170° C. ensued.

*Hydrogen Chloride Gas.*—Concentrated sulphuric acid was dropped from a separatory funnel into hydrochloric acid (concentrated) contained in a 3-liter flask. The evolved hydrogen chloride gas was dried and purified by passing it through two sulphuric acid drying bottles and a calcium chloride tower.

*Hydrogen Bromide Gas.*—Two methods of preparation were tried. (a) Bromine was dropped slowly upon red phosphorus

<sup>1</sup> Gattermann: "Practical Methods of Organic Chemistry," Trans. 1898, p. 324.

covered with water. To remove the excess of bromine the gas was passed through two U-tubes containing glass beads and red phosphorus. (b) Pure resublimed anthracene was substituted for the red phosphorus and water used in method a. Anthracene placed in U-tubes removed free bromine. All bromine used during this investigation was rectified by two distillations over manganese dioxide and sulphuric acid.

*Hydrogen Gas.*—Concentrated sulphuric acid (1 part) and water (3 parts) slightly colored by platinic chloride were allowed to act upon granulated zinc. The hydrogen was purified by its passage through a series of wash bottles containing (a) water or ammoniacal silver nitrate; (b) potassium permanganate; (c) alkaline lead nitrate; (d) and (e) sulphuric acid.

#### DESCRIPTION OF APPARATUS.

The gases prepared as described above were led through combustion tubes of hard glass in which were placed porcelain boats containing the material to be experimented upon. The exit end of the tube dipped either into a receiver containing water or into a U-tube containing sulphuric acid. The latter opened directly into a draft chamber. The combustion tube was heated over Bunsen burners provided with fish-tail attachments; an additional burner held in the hand served to supply extra heat when necessary.

A short arm Troemner balance, sensitive to the thirty-fifth of a milligram and a set of weights, carefully standardized were used for all weighings. In every instance the observed weight was reduced to the vacuum standard and the means of the series of determinations, the probable errors, etc., were calculated according to the formulas given by Clarke.<sup>1</sup>

All atomic weights used were taken from F. W. Clarke's annual report to the American Chemical Society for the current year.<sup>2</sup>

#### EXPERIMENTAL PART.

*I. Conversion of Silver Arsenate into Silver Chloride.*—It was shown by Moyer<sup>3</sup> that arsenic could be completely separated from

<sup>1</sup> F. W. Clarke: "Recalculation of the Atomic Weights," p. 7.

<sup>2</sup> F. W. Clarke: *This Journal*, 23, 94 (1901).

<sup>3</sup> Moyer: Thesis, University of Pennsylvania, 1896.



silver by heating silver arsenate in a current of hydrogen chloride gas. This fact was verified by the present author.

The method of procedure adopted was as follows: Dry silver arsenate was weighed out in a porcelain boat which was then placed in the combustion tube. A slow current of hydrogen chloride gas conducted through the tube gave rise to a vigorous reaction. Heat was evolved, the red-brown arsenate became yellowish white chloride and a deposit of water and arsenic trichloride appeared upon the inner walls of the tube. After half an hour a gentle heat was applied; when no further action could be observed the temperature was raised again, but not to such a degree as to cause the silver chloride to melt. At the close of the operation the silver chloride was barely fused, allowed to cool partially in the tube and then removed to a desiccator provided with anhydrous calcium chloride and soda lime. The desiccator and its contents were allowed to remain in the balance room for at least an hour before the boat was weighed. After weighing, the boat was reheated in a current of hydrogen chloride gas until the silver chloride was again fused. Cooling and weighing were carried out just as in the first instance. The analytical results follow:

Atomic weight of chlorine.....	35.45
Atomic weight of oxygen.....	16.00
Atomic weight of silver.....	107.92
Density of silver arsenate.....	5.77
Density of silver chloride.....	5.50

Silver arsenate. Grams.	Silver chloride. Grams.	Arsenic. Atomic weight.
0.23182	0.21547	74.987
0.47996	0.44615	74.944
0.52521	0.48820	74.956
0.80173	0.74517	74.996
0.94782	0.88083	75.061
1.02047	0.94830	75.083
1.03558	0.96258	74.974
1.05462	0.98014	75.033
Mean .....	75.004	
Probable error .....	±0.012	

*II. Reduction of Silver Chloride to Metallic Silver.*—The boat containing silver chloride, derived from silver arsenate as de-

scribed in the previous section, was covered with a strip of platinum foil (to prevent possible loss by spirting) and placed in a combustion tube connected with the hydrogen supply. After the air contained in the apparatus was expelled by hydrogen a very gentle heat was applied. Gradually the temperature was raised until the tube was at a red heat. In this condition it was maintained for at least half an hour. If great care was not exercised during the first part of the operation, loss by spattering was sure to occur. Five to seven hours were required for a reduction. The boat, its contents and its cover were allowed to remain in the desiccator at the temperature of the balance room at least an hour before weighing. Reheating to redness, cooling and weighing ensured complete reduction. The silver obtained was arsenic-free and completely soluble in nitric acid. Results are given herewith:

Atomic weight of oxygen.....	16.00
Atomic weight of silver.....	107.92
Density of silver arsenate.....	5.77
Density of silver.....	10.57

Silver arsenate. Grams.	Silver. Grams.	Arsenic. Atomic weight.
0.23182	0.162175	75.027
0.47996	0.33583	74.950
0.52521	0.367525	74.907
0.80173	0.56099	74.936
0.94782	0.66318	74.959
1.02047	0.71400	74.964
1.05462	0.73771	75.082
Mean .....		74.975
Probable error .....		$\pm 0.015$

*III. Conversion of Silver Arsenate into Silver Bromide.*—Silver arsenate was treated just as described under the first heading of the "Experimental Part" of this thesis, except that hydrogen bromide gas obtained from bromine and anthracene was substituted for hydrogen chloride gas. All due precautions against fusing were used, but it seemed that a little silver bromide always escaped when the last traces of arsenic were expelled. The weighing and other operations were conducted as outlined in previous sections. Variable results were obtained, most of them coming between 75.25 and 75.75. Two analyses yielded 74.984

and 74.967. The above determinations would serve well for ordinary quantitative analyses, but their lack of concordance bars them from use for atomic weight considerations. The silver bromide formed was arsenic-free.<sup>1</sup>

*IV. Conversion of Lead Arsenate into Lead Chloride.*—That arsenic could be completely eliminated from lead arsenate by the use of hydrogen chloride gas was proved by Hibbs<sup>2</sup>. In all of the following determinations, the lead chloride produced was examined for arsenic, but none was found.

Lead arsenate was weighed into porcelain boats. The boats and contents were heated to 150°-170° C. and again weighed. Hydrogen chloride gas was passed over the arsenate, at first in the cold, but afterwards at a gentle heat. A gradual increase in temperature was brought about and the current of gas was discontinued only after all action seemed to have ceased. In no case was the lead chloride fused. The usual precautions concerning cooling, weighing, reheating, etc., were followed out. The results obtained are:

Atomic weight of chlorine.....	35.45
Atomic weight of oxygen.....	16.00
Atomic weight of lead.....	206.92
Density of lead arsenate.....	6.29
Density of lead chloride.....	5.80

Lead arsenate. Grams.	Lead chloride. Grams.	Arsenic. Atomic weight.
0.38152	0.35381	74.988
0.436197	0.40449	75.016
0.57218	0.53065	74.964
0.60085	0.55717	75.020
0.74123	0.68736	75.010
0.77107	0.71494	75.067
0.88282	0.81858	75.054
0.97779	0.90674	75.054
Mean .....		75.022
Probable error .....		±0.009

Attempts were made to reduce lead chloride to metallic lead, by heating it in a current of hydrogen, but failed to give the desired

<sup>1</sup> Throughout the course of experiments it was found that the reactions in which hydrogen bromide was used gave more trouble than did those where hydrogen chloride was employed. Hydrogen iodide was more unsatisfactory than either of the preceding acids.

<sup>2</sup> Hibbs: *loc. cit.*

result. The temperature at which the chloride is reduced is so near that at which it is volatilized that the method is valueless. Careful heating for eight hours did not reduce all the lead chloride; some of it was found sublimed into the upper part of the boat. More lead chloride, mixed with black crystals of lead, was found adhering to the platinum cover placed over the boat.

*V. Conversion of Lead Arsenate into Lead Bromide.*—Preliminary experiments showed that the usual apparatus could be modified to advantage by inserting a stop-cock, through which air could be admitted to the combustion tube, in the neck of the U-tube preceding the combustion tube. By opening this cock the acid vapor could be diluted with air and thus the violence of the reaction was diminished. A filtering flask and suction pump attached to the exit receiver were also used.

The method employed in previous determinations was inapplicable here because the arsenic tribromide collecting in the boat was not readily expelled without loss due to spattering. The reaction took place violently in the cold, and bromine, water, and arsenic tribromide separated in large amounts.

As there were occasionally violent explosions when hydrogen bromide prepared from phosphorus, water and bromine was used,<sup>1</sup> and as phosphorus was found in the receiver, the method was abandoned for that employing anthracene and bromine. From this time no explosions occurred. Evidently the cause of the disturbance is to be looked for in the phosphorus used in the generator, hydrides of phosphorus being formed, rather than in the halide of arsenic, as was supposed by Meyer.<sup>2</sup>

The boat containing lead arsenate was placed in the combustion tube and heated to 200° C. Air mixed with hydrogen bromide was drawn through the apparatus and after all apparent action had ceased the heat was increased, but not to a point where fusion or volatilization of lead bromide could result. Cooling and weighing, reheating, cooling and weighing were carried out as usual. This manner of working prevented spattering, for the arsenic tribromide was removed as fast as it formed. The lead bromide was gray-white in color and contained no arsenic. Results follow:

<sup>1</sup> Chronologically this work preceded that described in Section III.

<sup>2</sup> Meyer: *This Journal*, 17, 735 (1895).

Atomic weight of bromine.....	79.95
Atomic weight of lead.....	206.92
Atomic weight of oxygen.....	16.00
Density of lead arsenate.....	6.29
Density of lead bromide.....	6.61

Lead arsenate. Grams.	Lead bromide. Grams.	Arsenic. Atomic weight.
0.59704	0.73092	75.066
0.61712	0.75567	74.967
0.65799	0.80569	74.980
Mean .....		75.004
Probable error .....		$\pm 0.021$

The lead bromide could not be reduced quantitatively for reasons analogous to those given for the non-reduction of lead chloride (see Section IV).

Many attempts were made to convert barium arsenate into barium chloride, magnesium pyroarsenate into magnesium chloride and sodium sulpharsenate and sodium cacodylate into sodium chloride, but the results were of such a nature as to be useless in fixing the atomic value under discussion and may well be omitted here.

A summary of the results obtained during the course of this investigation follows:

	Arsenic. Atomic weight.	Probable error.
$\text{Ag}_3\text{AsO}_4$ ——— $\text{AgCl}$	75.004	$\pm 0.012$
$\text{Ag}_3\text{AsO}_4$ ——— $\text{Ag}$	74.975	$\pm 0.015$
$\text{Pb}_3(\text{AsO}_4)_2$ — $\text{PbCl}_2$	75.022	$\pm 0.009$
$\text{Pb}_3(\text{AsO}_4)_2$ — $\text{PbBr}_2$	75.004	$\pm 0.021$
Mean.....	75.008	
Probable error.....	$\pm 0.006$	

This mean result, drawn from 26 determinations, affords another confirmation of the generally accepted atomic weight of arsenic. It may be interesting to note that 14 of the results lie below the general mean, while 12 of them lie above this value.

## LECTURE EXPERIMENTS ILLUSTRATING VARIOUS TYPES OF CATALYTIC ACTION.

A. A. NOYES AND G. V. SAMMET.

Received March 11, 1902.

### INTRODUCTION.

THE experiments to be described in this article were devised as an accompaniment to two lectures upon the subject of catalysis.<sup>1</sup> It has been decided to publish them, as it is believed that the series as a whole may be of value in connection with lecture courses on theoretical chemistry, and that some of the separate experiments might be introduced into courses on inorganic and organic chemistry.

The experiments are presented in such a manner as to make their preparation and performance as easy as possible for the lecturer. As this involves the enumeration of many details, those who desire to obtain only a general view of the experiments here described are recommended to read, under each experiment, only the paragraphs entitled "Catalyzer", "Reaction Catalyzed" and "Observations", omitting those designated "Preparation" and "Experiment".

In accordance with the proposal of Ostwald, we understand the term *catalysis* to signify the *acceleration or retardation of a chemical reaction by substances which themselves undergo no permanent change as a result of their action.*

For convenience of consideration we distinguish the following important types or classes of catalytic agents:

1. Carriers;
2. Adsorbent contact agents;
3. Electrolytic contact agents;
4. Water;
5. Dissolved electrolytes;
6. Enzymes;
7. Inorganic colloids.

### I. CATALYSIS BY CARRIERS.

By *carriers* are understood catalytic agents which are known to accelerate reactions through the formation of an intermediate compound with one of the reacting substances. Although it is

<sup>1</sup> Delivered before the North-eastern Section of the American Chemical Society and the Society of Arts of the Massachusetts Institute of Technology.

probable that some of the other types of catalytic agents (for example, enzymes) are in reality carriers, the term is here confined to those agents which are known to be such.

The experiments here described illustrate the action of carriers in the three states of aggregation, gaseous, liquid, and solid.

The suggestion of Wagner<sup>1</sup> that carrier-actions be designated pseudo-catalyses, thereby implying that they are not true cases of catalysis, seems to us an unfortunate one. There has always been a tendency to attach to the term catalysis a mysterious significance, which would be continued if the term is still to be confined to *unexplained* accelerating actions. The advantage of Ostwald's definition is that it is a concrete, experimental one, having no reference whatever to the way in which the acceleration is brought about.

#### *Experiment I.*

*Catalyser.*—Nitric oxide.

*Reaction Catalysed.*— $2\text{SO}_2 + \text{O}_2 = 2\text{SO}_3$ .

*Preparation of the Experiment.*—Graduate roughly, a long, narrow bell-jar of about 500 cc. capacity by marking lines upon it with a blue pencil at points corresponding to  $\frac{9}{18}$  and  $\frac{11}{18}$  of its total volume measured from the closed end of the jar. Rinse the jar with water so that the inner sides of it will be wet; fill it with mercury, and invert it over a long narrow trough, also filled with mercury, and having a deep longitudinal groove in the bottom. Introduce sulphur dioxide into the jar until the meniscus falls to the upper mark; then introduce, by means of a bent tube, enough water barely to cover the surface of the mercury. Connect the bent tube with a gasometer or cylinder of oxygen by means of a rubber tube. Fill two short, wide test-tubes with mercury, and invert them over the trough. Introduce into one of these tubes a volume of nitric oxide equal to 0.1 of the total volume of the bell-jar, and into the other tube one-half this amount of nitric oxide.

*Experiment.*—Introduce into the bell-jar oxygen from the gasometer or cylinder, until the mercury meniscus falls to the second mark. Place the mouth of the test-tube containing the larger amount of nitric oxide in the groove beneath that of the bell-jar,

<sup>1</sup> *Ztschr. phys. Chem.*, 28, 78.

and tip the tube until the gas has passed into the jar. After the mercury has nearly stopped rising, introduce in the same way into the jar the nitric oxide gas in the second tube.

*Observations.*—No change occurs on adding the oxygen to the sulphur dioxide. When the nitric oxide is introduced, the gas reddens and begins to contract and become filled with white fumes. A white deposit (nitrosylsulphuric acid) soon forms on the sides of the jar. The contraction nearly ceases after 30 to 40 seconds, but becomes rapid again when the second portion of the nitric oxide is introduced. The volume finally becomes constant at about 0.2 of the total volume of the jar.

### *Experiment 2.*

*Catalyzer.*—Sulphuric acid.

*Reaction Catalysed.*— $2\text{C}_2\text{H}_5\text{OH} = (\text{C}_2\text{H}_5)_2\text{O} + \text{H}_2\text{O}$ .

*Preparation of the Experiment.*—Connect a 500 cc. distilling flask with a Liebig condenser which is fitted with an adapter delivering into a 200 cc. graduate. Place in the flask 135 cc. of concentrated sulphuric acid, and add slowly 75 cc. of alcohol. Insert a 2-hole rubber stopper holding a thermometer and a 150 cc. drop-funnel, both of which reach nearly to the bottom of the flask. Fill the drop-funnel with alcohol, and, just before the lecture, heat the liquid in the flask to  $140^\circ$ - $150^\circ$ ; then allow the alcohol to flow slowly into the flask at such a rate that the distillate drops rapidly into the graduate.

*Experiment.*—Add to the ether which has collected in the graduate 2 cc. of powdered potassium carbonate, and shake. After the layers have formed pour the top layer into a 200 cc. graduate which contains 75 cc. of water, and shake.

*Observations.*—The alcohol is continuously converted to ether, which comes over in the distillate and holds the water which is also produced by the reaction in solution; but on adding the potassium carbonate the distillate separates into two layers consisting of about 5 cc. of water to 100 cc. of ether. On pouring the upper layer into water, it does not mix with it, showing that the distillate is mainly ether, and not alcohol.



*Experiment 3.*

*Catalyser.*—Ferric bromide.

*Reaction Catalyzed.*— $C_6H_6 + Br_2 = C_6H_5Br + HBr$ .

*Preparation of the Experiment.*—Support a 250 cc. distilling flask upon a lamp-stand and connect its side-arm with a funnel whose mouth dips just below the surface of a caustic potash solution. Place in the flask 4 cc. of bromine. Provide a cork stopper for the flask, a long-necked funnel, a small wash-bottle, like that used in Experiment 2, containing strong ammonia, 30 cc. of benzene in a small bottle, and 0.5 cc. of powdered iron.

*Experiment.*—Pour into the distilling flask the 30 cc. of benzene; then add the 0.5 cc. of powdered iron. Blow ammonia gas from the wash-bottle over the neck of the distilling flask. Finally insert the cork.

*Observations.*—No action occurs between the benzene and bromine alone, but a vigorous boiling up and great clouds of white fumes are observed as soon as the iron is added.

*Experiment 4.*

*Catalyser.*—Aluminum chloride.

*Reaction Catalyzed.*— $C_6H_6 + CH_3COCl = C_6H_5COCH_3 + HCl$ .

*Preparation of the Experiment.*—Place a 250 cc. distilling flask in a clamp on a lamp-stand. Connect the side-arm with a funnel that dips just beneath the surface of a potash solution. Pour into the flask 10 cc. of acetyl chloride. Provide a cork stopper for the flask, a long-necked funnel, 50 cc. of benzene in a small bottle, 10 cc. of powdered sublimed aluminum chloride in a corked test-tube, and a small wash-bottle of strong ammonia with a rubber syringe bulb attached to the longer tube.

*Experiment.*—Pour into the flask through the funnel the 50 cc. of benzene, then add the 10 cc. of aluminum chloride. Blow from the wash-bottle ammonia gas over the mouth of the flask, and finally insert the cork.

*Observations.*—No action occurs between the benzene and acetyl chloride alone, but a vigorous effervescence and copious evolution of white fumes occur soon after the aluminum chloride is added.

*Experiment 5.*

*Catalyzer.*—Platinum foil.

*Reaction Catalyzed.*— $2\text{CH}_3\text{OH} + \text{O}_2 = 2\text{CH}_2\text{O} + \text{H}_2\text{O}$ .

*Preparation of the Experiment.*—Pour into a 300 cc. beaker a layer of methyl alcohol 1 cm. deep. Cover the beaker with a perforated watch-glass in whose perforation is a cork stopper from which a star made of platinum foil hangs down by a platinum wire 2 to 3 cm. above the surface of the alcohol.

*Experiment.*—Ignite the methyl alcohol vapor in the beaker by applying the flame of a burner to it, and raise one side of the watch-glass a few millimeters by inserting a bit of wood or rubber tube.

*Observations.*—The platinum star glows brightly when the amount of air admitted to the beaker is properly adjusted.

## 2. CATALYSIS BY ADSORBENT CONTACT AGENTS.

By adsorbent contact agents we understand solid substances that accelerate reactions by the adsorption on their surfaces of one or more of the reacting substances. Whether the acceleration is due to an increase in the concentration of the reacting substances, or to an activation of them, or to a chemical combination constituting a carrier action, is not thereby taken into consideration.

The experiments to be here presented refer mostly to gaseous mixtures, but include one dissolved substance (hydrogen peroxide).

*Experiment 6.*

*Catalyzer.*—Platinum.

*Reaction Catalyzed.*— $2x\text{NH}_3 + y\text{O}_2 = 3x\text{H}_2\text{O} + z\text{N}_2 + w\text{NO}$ .

*Preparation of the Experiment.*—Place in a wide-necked bottle of about 250 cc. capacity, 75 cc. of concentrated ammonia-water (sp. gr., 0.90). Insert a delivery tube, which is connected to a tank of oxygen, so that it dips below the surface of the ammonia-water. Wind one end of a platinum wire (about 0.5 mm. diameter) around a match, leaving the other end so long that, when the match is supported across the mouth of the bottle, the end will be about 1 cm. above the surface of the liquid.

*Experiment.*—Heat the platinum wire in a flame, and insert it while hot into the flask. After a few seconds turn on a moderately rapid current of oxygen.

*Observations.*—Almost immediately after introducing the platinum wire into the flask, it begins to glow. When the oxygen is bubbled through the ammonia, the platinum glows more brightly, and the flask becomes filled with white fumes; and after a few seconds an explosion is produced.

#### *Experiment 7.*

*Catalyzer.*—Platinum.

*Reaction Catalyzed.*— $2\text{SO}_2 + \text{O}_2 = 2\text{SO}_3$ .

*Preparation of the Experiment.*—Place about 5 grams of loose asbestos on a filter plate and pour through it a 10 per cent. hydrochloroplatinic acid solution until the asbestos is saturated with it. Transfer it to a large porcelain crucible, and ignite strongly for thirty minutes, disintegrating the mass from time to time. Pack loosely with the platinized asbestos a piece of combustion tubing about 45 cm. long, to within 4 or 5 cm. of one end and 20 cm. of the other. Place the tube in a short furnace with 2 or 3 burners, and connect one end by means of rubber stoppers and a delivery tube to one of the necks of a three-necked Woulff bottle which is charged to a depth of 2 or 3 cm. with concentrated sulphuric acid. The other two necks of the Woulff bottle are connected by means of rubber stoppers and delivery tubes which dip below the surface of the sulphuric acid in the Woulff bottle, to an oxygen cylinder and a sulphur dioxide generator, respectively. The sulphur dioxide is produced by dropping strong sulphuric acid from a drop funnel into a flask containing strong commercial sodium bisulphite solution. The other end of the combustion tube is fitted with a rubber stopper carrying a T-tube, of which the perpendicular arm is closed by a piece of rubber tubing and a pinch-cock. The straight end of the T-tube is joined to a condensation-tube (such as is used for sulphur dioxide), the bulb of which is placed in a dish of ice. The outlet of the condensation-tube is connected to a funnel, the mouth of which dips only a little below the surface of a potash solution.

*Experiment.*—Pass the oxygen and sulphur dioxide at a moderate rate through the tube so that the sulphur dioxide bubbles through the sulphuric acid about twice as fast as the oxygen. Light the burners beneath the empty part of the tube, and heat it to just below redness; after a minute or two, open the pinch-cock momentarily to show that no combination is taking place. Then push the tube along so that the platinized asbestos is brought over the flame, and, after the tube has become hot, open the pinch-cock on the T-tube for a moment. Continue the experiment for fifteen minutes or more, and then remove the condensation-tube from the ice-bath.

*Observations.*—No white fumes are seen on opening the pinch-cock until the platinized asbestos is heated. After about fifteen minutes the condensation-tube will be coated with white crystals.

### *Experiment 8.*

*Catalyzers.*—Platinum black and bone-black.

*Reaction Catalyzed.*— $2\text{H}_2\text{O}_2 = 2\text{H}_2\text{O} + \text{O}_2$ .

*Preparation of the Experiment.*—Place in each of two lecture test-tubes 25 cc. of commercial, concentrated hydrogen peroxide solution which has been made very slightly alkaline by the addition of ammonia. Soak two 9-cm. filter-papers in a 10 per cent. hydrochlorplatinic acid solution; dry the filter papers and ignite them in a large porcelain crucible until the carbon is all burned off. Place the reduced platinum in a small test-tube. Provide also 1 cc. of bone-black and a splinter of wood.

*Experiment.*—Add the reduced platinum to one portion of hydrogen peroxide solution and the bone-black to the other portion. Ignite the wood-splinter in a flame until one end of it glows when removed from the flame, and insert it in turn into each of the test-tubes.

*Observations.*—When the platinum black and the bone-black are added to the hydrogen peroxide a violent effervescence ensues and the glowing splinter becomes ignited.

### 3. CATALYSIS BY ELECTROLYTIC CONTACT AGENTS.

Electrolytic contact agents are those catalytic agents which

accelerate reactions in which metals are involved through the formation of a voltaic couple. They are themselves in all cases metallic substances. Two experiments are given below, illustrating their action in case of an inorganic and of an organic reaction, respectively.

#### *Experiment 9.*

*Catalyser.*—Platinum.

*Reaction Catalysed.*— $\text{Sn} + 2\text{HCl} = \text{SnCl}_2 + \text{H}_2$ .

*Preparation of the Experiment.*—Fit a 300 cc. Erlenmeyer flask with a rubber stopper provided with a thistle-tube and a delivery-tube, the end of which dips into a beaker of water. Cover the bottom of the flask to a depth of 2 cm. with a layer of pure feathered tin. Provide a medicine dropper, some hydrochloric acid of 1.12 sp. gr., and a little 10 per cent. hydrochlorplatinic acid solution.

*Experiment.*—Pour into the flask through the thistle-tube enough hydrochloric acid to entirely cover the tin; then add 5 or 6 drops of the platinum solution and shake.

*Observations.*—Only a very slight action occurs between the tin and acid alone; but a vigorous effervescence and rapid evolution of gas occur soon after the platinum solution is added.

#### *Experiment 10.*

*Catalyser.*—Copper.

*Reaction Catalysed.*— $\text{C}_2\text{H}_4\text{Br}_2 + \text{Zn} = \text{C}_2\text{H}_4 + \text{ZnBr}_2$ .

*Preparation of the Experiment.*—Place 20 cc. of absolute alcohol and 20 cc. of ethylene bromide in a lecture test-tube whose mouth is fitted with a cork carrying a straight piece of (5 mm. wide) delivery tubing. Provide 2 cc. of granulated zinc in a test-tube, a little saturated solution of crystallized copper chloride in alcohol, and a beaker of ice water.

*Experiment.*—Pour the zinc into the test-tube, then add 3 cc. of the copper chloride solution, insert the cork, and shake. As soon as the effervescence becomes very vigorous, so that the air has been completely expelled, light the gas issuing from the tip of the

delivery tube. When the action becomes too violent, place the test-tube in the beaker of ice water.

*Observations.*—No action occurs between the ethylene bromide and zinc alone, but a vigorous effervescence begins in about ten or fifteen seconds after the addition of the copper chloride, and a large jet of flame is produced when the gas is ignited.

#### 4. CATALYSIS BY WATER.

Water is a substance whose presence in at least minute amounts seems to be essential to the occurrence of most chemical reactions. Moreover, its method of action is probably unique, consisting either in a hydration or electrolytic dissociation of the reacting substance. It is therefore not inappropriate that it alone constitutes a type of catalytic agent.

Four experiments illustrating its action on gaseous, liquid, and solid reacting mixtures, and on a solid-gaseous mixture, are here described.

#### *Experiment II.*

*Catalyser.*—Water.

*Reaction Catalysed.*— $2\text{H}_2\text{S} + \text{SO}_2 = 2\text{H}_2\text{O} + 3\text{S}$ .

*Preparation of the Experiment.*—Fit a thoroughly dry glass balloon with a cork stopper with four holes carrying two dry delivery tubes leading to the bottom of the balloon and a third one terminating just below the stopper. All of these tubes should be bent at right angles above the stopper. Connect one of the long tubes with a tower filled with calcium chloride, which in turn is connected with a gas wash-bottle containing dilute sulphuric acid (1:3), which last is connected with a Kipp hydrogen sulphide generator. Connect the other long tube through two gas wash-bottles containing concentrated sulphuric acid, with a sulphur dioxide gasometer, or a generator in which sulphur dioxide is made by dropping concentrated sulphuric acid into a strong solution of commercial acid sodium sulphite. Connect the third delivery tube with a funnel whose mouth dips a little below the surface of a strong caustic potash solution. Close the fourth hole of the stopper with a piece of glass rod. Pass the two gases into the

balloon for ten to fifteen minutes, running the hydrogen sulphide about twice as fast as the sulphur dioxide. (The experiment may fail if the sulphur dioxide is in considerable excess.) Place a 250 cc. flat-bottom flask upon a tripod with a burner beneath. Fill it one-third full of water and fit it with a rubber stopper provided with a delivery tube, so bent that its outer end can be easily inserted in the fourth hole of the stopper of the balloon. Regulate the flame of the burner so that the water is kept barely boiling.

*Experiment.*—Cause the two gases to flow into the balloon for half a minute. Then remove the piece of glass-rod, insert the delivery tube leading from the flask of boiling water, and allow the steam to flow into the balloon for a few seconds.

*Observations.*—Nothing occurs on mixing the two gases in the dry state. After introducing the steam, sulphur at once begins to deposit on the walls of the balloon, and, in the course of half a minute, completely covers them.

### *Experiment 12.*

*Catalyser.*—Water.

*Reaction Catalysed.*— $I_2 + H_2S = 2HI + S$ .

*Preparation of the Experiment.*—Place 250 cc. of commercial sodium-distilled ether in a 500 cc. glass-stoppered bottle. Dissolve in this 0.35 gram of iodine and saturate the solution with hydrogen sulphide by passing through it for ten minutes a slow current of gas, generated in a Kipp generator and dried by being passed first through a gas wash-bottle containing dilute sulphuric acid (1:3) and then through a drying tower filled with calcium chloride. Place the hydrogen sulphide apparatus upon the lecture table. Measure out 3 cc. of water in a small graduate.

*Experiment.*—Pass a slow current of hydrogen sulphide into the ethereal solution of iodine for half a minute. Add 3 cc. of water to the ether solution and shake thoroughly.

*Observations.*—Decolorization of the dry ethereal solution of iodine is caused only very slowly by the hydrogen sulphide, but takes place very rapidly when the water is added.

*Experiment 13.*

*Catalyzer.*—Water.

*Reaction Catalyzed.*— $\text{Zn} + \text{I}_2 = \text{ZnI}_2$ .

*Preparation of the Experiment.*—Place 4 cc. of powdered iodine in a test-tube and 2 cc. of zinc dust in a 25 cc. glass-stoppered wide-mouthed bottle. Place a carbon-funnel in the mouth of a 4-liter glass balloon supported on a suitable ring. Provide a wash-bottle delivering a fine stream.

*Experiment.*—Pour the iodine into the bottle containing the zinc dust and shake. Then pour the mixture onto the bottom of the balloon and direct a stream from the wash-bottle upon it.

*Observations.*—On the addition of water to the dry mixture of the zinc dust and powdered iodine, a violent action takes place attended by a sizzling and evolution of violet vapors of iodine, which entirely fill the balloon.

*Experiment 14.*

*Catalyzer.*—Water.

*Reaction Catalyzed.*— $2\text{Na} + \text{Cl}_2 = 2\text{NaCl}$ .

*Preparation of the Experiment.*—Fill a piece of combustion tube 100 cm. long, which has been dried by flashing with a flame, quickly with phosphorus pentoxide for  $\frac{2}{3}$  of the distance from one end of the tube, using ignited asbestos plugs to hold it in place. The delivery tube from a gasometer of chlorine is joined to a T-tube, one branch of which is connected with a rubber tube (provided with a pinch-cock) long enough to reach to the empty end of the combustion tube; the other branch of the T-tube leads through two gas-wash-bottles containing sulphuric acid to the filled end of the combustion tube, which is fitted with a rubber stopper carrying a Y-tube, of which the third branch leads through a rubber tube provided with a pinch-cock to a funnel dipping under strong caustic potash solution. Fit the empty end of the combustion tube with a perforated stopper carrying a small delivery tube. Pass chlorine at a slow rate for half an hour through the sulphuric acid bottles and the combustion tube, which is inclined somewhat so that the gas enters at the lower end.



While the chlorine is passing, flash the empty part of the combustion tube for some minutes with a flame in order to dry it completely. Provide a Bunsen burner, a small porcelain boat, a pair of pincers, several pieces of sodium of the size of a pea, and a stout wire with a hook at one end for removing the boat from the combustion tube.

*Experiment.*—Start a slow current of chlorine through the combustion tube. Place in the porcelain boat three or four pieces of sodium. Ignite the sodium by heating the boat in the flame of the burner and push it into the empty part of the combustion tube. Draw the boat back into the air for a moment, and again push it into the tube; then insert the stopper, connect the delivery tube in it with the rubber tube leading directly to the chlorine generator, and open the pinch-cock upon it. Open the pinch-cock on the tube leading into the potash solution, and pass a rapid current of the undried chlorine over the sodium through the tube in the reverse direction to that of the previous current.

*Observations.*—When the burning sodium is inserted in the dry chlorine, it is extinguished. When drawn back into the air, it becomes again ignited, and is again extinguished on pushing it back into the dry chlorine. When the moist chlorine is passed over it, it burns with great brilliancy.

##### 5. CATALYSIS BY DISSOLVED ELECTROLYTES.

Dissociated substances in aqueous solution exert a variety of catalytic actions. The most important of these is that exerted upon reactions of hydrolysis by acids in virtue of their hydrogen ions.<sup>1</sup> This is illustrated by an experiment on the saccharification of starch by sulphuric acid.

Another variety of catalytic action by electrolytes is the great retardation of reactions involving weak acids, by their neutral salts,—a phenomenon explained by the Ionic Theory and the Law

<sup>1</sup> We desire to take this opportunity to suggest what seems to us a plausible hypothesis in regard to the action of hydrogen ions: that is, that these ions are hydrated and that the water in combination with them is more reactive than ordinary water; in other words, that the hydrogen ions act as water-carriers. While there is at present no experimental evidence in favor of this hypothesis (or of any other), the fact that it is an entirely reasonable one shows that one of the purest types of catalytic action may be in reality only a carrier action.

of Mass-Action. A lecture experiment illustrating this has been already described in detail in this Journal.<sup>1</sup>

Still another variety of such catalytic actions is the highly specific influence on reactions of oxidation and reduction of certain dissociated substances, especially of those which are themselves capable of undergoing oxidation or reduction. An experiment on a reaction of this kind has been earlier presented.<sup>2</sup>

Finally is to be mentioned a type of action which electrolytes exert apparently as a direct consequence of the electric charges upon the ions, namely, the coagulation of colloidal solutions and fine suspensions. Although this is not in a strict sense a catalytic action, since according to recent experiments<sup>3</sup> a minute quantity of the electrolyte is decomposed and precipitated with the colloid, yet the coagulative effect produced is so great in comparison with the quantity of electrolyte consumed that it has, from a practical standpoint, the characteristics of a catalysis. We have therefore included an experiment showing both the coagulation of colloidal arsenic sulphide by salts and the much greater coagulating effect upon it of bivalent than of univalent positive ions.

### *Experiment 15.*

*Catalyzer.*—Sulphuric acid.

*Reaction Catalyzed.*— $(C_6H_{10}O_5)_x + xH_2O = xC_6H_{12}O_6$ .

*Preparation of the Experiment.*—Place 2 cc. of starch in each of two lecture test-tubes. Measure out in small graduates two 5 cc. portions of Fehling's solution, 25 cc. of a 5 per cent. sulphuric acid solution and enough strong caustic potash solution to neutralize this acid (9 cc. of 50 per cent. potash).

*Experiment.*—Add the 25 cc. of acid to the starch in one of the test-tubes and 25 cc. of water to that in the other, and boil both for about half a minute. Neutralize the acid solution with the potash. Bring the contents of both test-tubes to a boil, then add 5 cc. of Fehling's solution to each, and bring to a boil again.

*Observations.*—On addition of the Fehling's solution a heavy

<sup>1</sup> This Journal, 22, 744.

<sup>2</sup> *Ibid.*, 22, 742.

<sup>3</sup> Linder and Picton: *J. Chem. Soc.*, 67, 63 (1895); Whitney and Ober: This Journal, 23, 842 (1901).

red precipitate is thrown out in the tube in which the starch was boiled with the acid, but the blue color of the solution is not discharged in the other tube containing only starch and water.

### *Experiment 16.*

*Catalyzers.*—Barium chloride and sodium chloride.

*Reaction Catalyzed.*— $\text{As}_2\text{S}_3$  (colloid) =  $\text{As}_2\text{S}_3$  (precipitate).

*Preparation of the Experiment.*—Saturate 250 cc. of cold distilled water with hydrogen sulphide, and add to it gradually (that is, within two or three minutes) a solution of 5 grams of arsenious oxide in 250 cc. of water, keeping the hydrogen sulphide passing into the solution during the addition. Filter this solution. Place 200 cc. of it in each of two lecture jars provided with glass stirring rods. Prepare 100 cc. of a half-normal solution of barium chloride and also of one of sodium chloride.

*Experiment.*—Add to the colloid in one jar 3 cc. of the barium chloride solution, stirring constantly. To the other colloid, add 25 cc. of the sodium chloride solution, and after waiting about a minute, add 40 cc. more.

*Observations.*—On addition of the salt solutions to the colloid, immediate coagulation of arsenious sulphide takes place in the solution to which the barium chloride was added, and on waiting a minute or so, the precipitated sulphide settles in this solution, while no change takes place in the colloid to which the sodium chloride was added. On the addition of the second portion of sodium chloride, however, this solution also coagulates.

## 6. CATALYSIS BY ENZYMES.

Enzymes are complex organic substances of animal or vegetable origin which exert a variety of catalytic actions. Enzymes may be classified as hydrolyzing, oxidizing, molecule-splitting, synthesizing, and coagulating, according to the nature of the reaction which they catalyze. Experiments are described below illustrating the first, third, and fifth of these classes; namely, the hydrolysis of starch by ptyalin and of a glucoside by emulsin, the decomposition of hydrogen peroxide by blood, and the coagulation

of casein by rennet. The decomposition of hydrogen peroxide is produced by enzymes of all kinds, and is therefore not a good example of a specific molecule-splitting enzyme. A far better one would be the decomposition of sugar into alcohol and carbon dioxide by zymase, the recently discovered enzyme to which the action of yeast has been shown to be due; but its separation from the yeast-cells is a matter of some difficulty.<sup>1</sup> The hydrogen peroxide experiment is introduced here partly for the sake of illustrating the retarding effect which poisons exert on enzyme-action.

### Experiment 17.

*Catalyzer.*—Ptyalin.

*Reaction Catalyzed.*— $(C_6H_{10}O_5)_x + xH_2O = xC_6H_{12}O_6$ .

*Preparation of the Experiment.*—Place in a lecture test-tube an amount of corn-starch of the volume of a split pea. Provide 25 cc. of fresh saliva and a little 1 per cent. iodine solution. (Secretion of saliva in the mouth may be greatly promoted by chewing a piece of paraffin.)

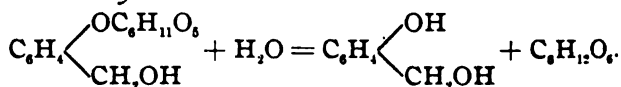
*Experiment.*—Add 10 cc. of water to the starch and heat it to boiling. Add 10 cc. more of cold water and 2 or 3 drops of the iodine solution; then add the 25 cc. of saliva. When decolorized, add a few more drops of iodine.

*Observations.*—The starch solution becomes of a deep blue color on the addition of the iodine, and this disappears almost immediately on addition of the saliva and is not restored when the second portion of iodine is added.

### Experiment 18.

*Catalyzer.*—Emulsin.

*Reaction Catalyzed.*—



*Preparation of the Experiment.*—Dissolve 10 cc. of powdered salicine in 75 cc. of water. Place half of this solution in each of

<sup>1</sup> See Effront: "Enzymes and their Applications," Prescott's Translation, p. 277.

two lecture test-tubes. Rub 0.25 gram of emulsin to a fine powder in a mortar and treat it with 20 cc. of warm water; allow it to stand for some hours and then filter it. Pour one-half of the emulsin solution into each of two small test-tubes. Measure out two 5 cc. portions of Fehling's solution.

*Experiment.*—Add to one of the test-tubes containing the salicine one-half of the solution of emulsin, warm gently (not above  $50^{\circ}$ ), and allow to stand for more than a minute. In the meantime, heat the rest of the emulsin to boiling for half a minute, add it to the other half of the salicine, and heat the mixture to boiling. Then heat the other tube of salicine and emulsin to boiling, add 5 cc. of Fehling's solution to each tube, and bring to a boil again.

*Observations.*—On boiling with Fehling's solution, scarcely any change takes place in the salicine solution to which the emulsin destroyed by boiling was added, but decolorization and formation of a red precipitate take place in the other salicine solution which was treated with the unboiled emulsin.

#### *Experiment 19.*

*Catalyzers.*—Blood and blood + potassium cyanide.

*Reaction Catalyzed.*— $2\text{H}_2\text{O}_2 = 2\text{H}_2\text{O} + \text{O}_2$ .

*Preparation of the Experiment.*—Place in each of two lecture test-tubes 25 cc. of hydrogen peroxide. Provide 2 cc. of saturated potassium cyanide solution, some fresh blood, and a medicine dropper.

*Experiment.*—To one tube of hydrogen peroxide add 5 or 6 drops of the potassium cyanide solution, then add to each tube 4 or 5 drops of blood.

*Observations.*—A very vigorous effervescence and a voluminous frothing occur in the tube of hydrogen peroxide to which blood alone was added, while in the one to which the cyanide was added only a slight action takes place.

#### *Experiment 20.*

*Catalyser.*—Rennet.

*Reaction Catalyzed.*—Casein (colloid) = Casein (precipitate).

*Preparation of the Experiment.*—Place 200 cc. of skimmed milk in a lecture jar. Provide some commercial liquid rennet.

*Experiment.*—Add 30 cc. of the rennet to the milk, and stir.

*Observations.*—Almost immediate coagulation of the milk occurs.

## 7. CATALYSIS BY INORGANIC COLLOIDS.

### *Experiment 21.*

*Catalyzers.*—Colloidal platinum and colloidal platinum + potassium cyanide or iodine.

*Reaction Catalyzed.*— $2\text{H}_2\text{O}_2 = 2\text{H}_2\text{O} + \text{O}_2$ .

*Preparation of the Experiment.*—Prepare some colloidal platinum solution as follows:<sup>1</sup> Attach each of two short platinum wires 1 mm. in diameter, to a stout copper wire, covered with insulating material, by binding the ends of the copper and platinum wire together with thin copper wire. Slip a small glass tube over each platinum wire so as to cover it within 1 cm. of its free end. Connect the wires with the terminals of a 110-volt-direct-circuit, having a 32-candle-power lamp in series. Place pure distilled water, best that distilled from alkaline permanganate, in a crystallizing dish 10 cm. in diameter, and surround this dish, in a larger one, with cracked ice and water. Grasp the glass tubes firmly in the hand, bring the two platinum points together beneath the surface of the pure water, and immediately separate them so as to form an arc. Maintain this arc for about ten minutes, pulling the platinum points apart when they fuse together and touching them momentarily when the arc disappears as a result of too great separation of the wires. Filter the black solution thus obtained and keep it in a stoppered bottle. Place in each of two lecture test-tubes 25 cc. of hydrogen peroxide made slightly alkaline with ammonium hydroxide. Provide 2 cc. saturated potassium cyanide solution, 2 cc. 5 per cent. solution of iodine in potassium iodide, two 10 cc. graduated, and a medicine dropper.

*Experiment.*—Measure out two 10 cc. portions of the colloidal platinum solution, and add to one portion about 5 drops of the

<sup>1</sup> According to Bredig's directions. See *Ztschr. phys. Chem.*, 31, 271 (1900).

potassium cyanide solution. Pour one of these two portions into each of the tubes of hydrogen peroxide. After a vigorous effervescence has started in the solution which contains no cyanide, add about 5 drops of the iodine solution to it.

*Observations.*—After the hydrogen peroxide has stood about a minute with the colloidal platinum solution, a vigorous effervescence occurs in the solution which contains no potassium cyanide, while in the solution in which the cyanide is present no appreciable evolution of gas occurs. Immediately after adding the iodine to the effervescing tube, the reaction slackens, and in the course of a few seconds the evolution of oxygen almost entirely ceases.

MASSACHUSETTS INSTITUTE OF TECHNOLOGY.

---

[CONTRIBUTIONS FROM THE LABORATORY OF THE BUREAU OF CHEMISTRY  
No. 44. SENT BY H. W. WILEY.]

## THE POLARIZATION OF FRUITS, JELLIES, JAMS, AND HONIES.

BY L. M. TOLMAN.

Received March 8, 1902.

LARGE amounts of sucrose are added in the preparation of jellies and jams, some of which is inverted in the process by the action of the organic acids, such as citric, malic, or tartaric. As a rule the jams which are cooked the longest<sup>1</sup> show the largest amount of inversion as would be expected. In working with a large number of these products, however, the rather curious fact was noted that apparently complete inversion rarely if ever took place, or, at least, in polarizing before and after inversion there was always an increase in the minus reading on the sugar scale, often not more than from 1° to 2°, which calculated as sugar by the Clerget formula showed from 1 to 1.5 per cent. of cane sugar. The usual explanation of the phenomenon is that it is due to cane sugar, but it is probable that this change is due to an entirely different cause.

It must be remembered that the cane sugar in these products has been inverted by the action of the fruit acids and it is possible

<sup>1</sup> Tolman, Munson, and Bigelow: *This Journal*, 22, 351 (1901).

to show by some investigations made by myself recently that this change in polarization is due to the action of hydrochloric acid on the invert sugar present. What this action is has never been explained, but it is a well-known fact that the simple presence<sup>1</sup> of hydrochloric acid increases the rotatory power of invert sugar. This is shown in the following table from Lippmann<sup>2</sup> in which is noted the effect on the polarization of an invert sugar solution at 20°, of different amounts of hydrochloric acid.

TABLE I.

Weight of sugar Grams.	Polarization Ventske degrees.			
	5 cc. HCl.	10 cc. HCl.	15 cc. HCl.	20 cc. HCl.
26.048	— 34.00	— 35.04	— 35.95	— 36.80
13.024	— 33.00	— 34.12	— 35.15	— 36.03

Lippmann's polarizations were all made at 20° C., and in the case of the half-normal weight the reading was multiplied by 2 for comparison. This table shows that hydrochloric acid, by its simple presence, affects the polarization. It is but logical to suppose that, if each succeeding 5 cc. of the hydrochloric acid affected the polarization, the first 5 cc. must also, and that if an inversion were made without any acid present the reading would be still less.

In order to demonstrate this fact, *i. e.*, that an addition of hydrochloric acid increases the rotation of invert sugar, especially with regard to such invert sugar as has been prepared with organic fruit acids, and honey in which the sugar has perhaps been inverted in the digestive tract of the bee, and to justify the expectation that in making a polarization, before and after inversion, with these substances a change in reading of 1° or 2° would take place even when no sucrose was present, the following experiment was undertaken.

(It might be well to say in the beginning that all the polarizations were made in a water-jacketed tube and in that way the temperature was very exactly controlled. In most of the polarizations the greatest change in temperature was not more than 0.2° C., and correction was made for that difference.)

A strong solution of cane sugar was taken and inverted with nitric acid (2 grams to 100 cc.) by boiling for one-half hour.

<sup>1</sup> H. A. Weber: *This Journal*, 17, 321, et seq.

<sup>2</sup> Lippmann: "*Chemie die Zuckerarten*," p. 800.



Fifty cc. portions were measured into 100 cc. flasks and each test was run in a duplicate, the average of a number of readings being taken.

One set of 2 flasks was made up to volume with distilled water. To another set 5 cc. of hydrochloric acid (sp. gr. 1.20) was added, the volume made up to 75 cc. and heated to 67° C., in fifteen minutes, according to the directions for the inversion of cane sugar used by the Association of Official Agricultural Chemists. To a third set 10 cc. of hydrochloric acid were added and treated as in the previous case. To a fourth and fifth set 5 and 10 cc. of hydrochloric acid were added and they were at once made up to volume in the cold and polarized, giving the acid practically no chance to exert any inverting action.

The second and third sets were cooled, made up to volume, and polarized. The results obtained are shown in Table II.

TABLE II.

Description of sample.		Ventzke °.	Temper-	Change in
		Polarization	ature. °C.	rotation.
No. 1.	Containing no HCl.....	- 23.0	18.0	..
No. 2.	Containing 5 cc. HCl, 67° C.....	- 24.2	18.4	1.2
No. 3.	Containing 10 cc. HCl, 67° C.....	- 25.0	17.8	2.0
No. 4.	Containing 5 cc. HCl (cold) . . .	- 24.2	18.4	1.2
No. 5.	Containing 10 cc. HCl (cold) . . .	- 25.0	18.0	2.0
No. 6.	Containing 10 cc. HCl (N/4) (cold)	- 23.4	18.0	0.4

From this table it will be seen that it makes practically no difference whether the solutions are heated in order to invert any sucrose present or whether the acid is simply added and polarized before there could be practically any inversion. It is hardly possible to say that there had been immediate inversion in the cold by the acid of a small amount of sucrose present to account for the change in rotation caused by the acid in the cold, as it is well known that hydrochloric acid inverts very slowly in the cold.

It seems evident enough that the presence of hydrochloric acid increases the levo-rotatory power of invert sugar as shown in Table II, from the comparative effects of the 5 cc. and the 10 cc. of strong hydrochloric acid and of the weak N/4 hydrochloric acid.

This experiment is made under practically the same conditions as are present in jam in which the sucrose had been inverted with some fruit acid. The direct polarization is made, the hydrochloric

acid added to cause the inversion, and there is an increase of rotation to the left of from  $1^\circ$  to  $2^\circ$ , depending on the amount of invert sugar present and the amount of hydrochloric acid added. Calculated as cane sugar, this change amounts to from 1 to 1.5 per cent., whereas in reality there is no sucrose present and the change in rotation has been due to the causes explained above. The same conditions are present in honey in which there is a large amount of invert sugar. But even in case the inversion has been effected by hydrochloric acid and this acid is still present, the simple addition of more hydrochloric acid, as is shown in Tables I and II, causes an increased rotation. For these reasons it is not possible

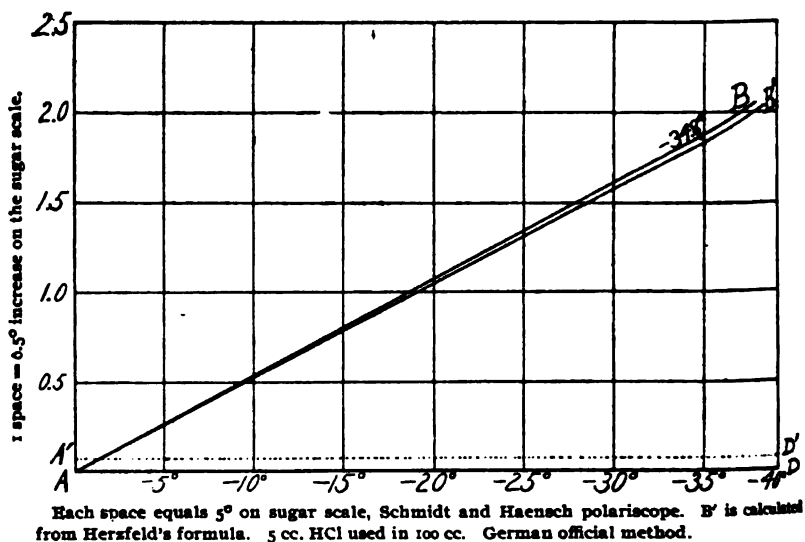
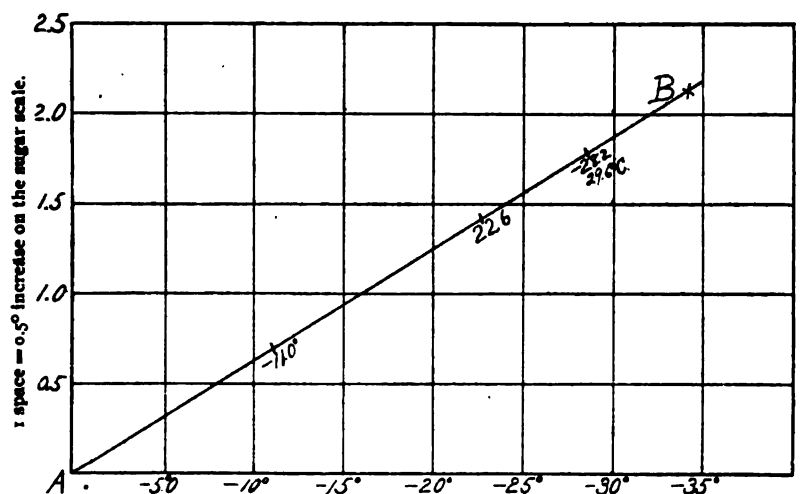


Fig. 1.

to make any accurate determination, by polarization, before and after inversion, and the calculation by the Clerget formula, of a small amount of cane sugar in the presence of a large amount of invert sugar, unless a correction can be introduced to compensate for this action. The writer has endeavored to construct a formula which would correct this error. In order to show clearly the basis of the proposed correction, it is necessary to consider first Figs. 1 and 2 and the Herzfeld formula.



Each space = 5° on sugar scale of Schmidt and Haensch polariscope. 10 cc. HCl in 110 cc. Method of Association of Official Agricultural Chemists.

Fig. 2.

Fig. 1 shows graphically the effect of the hydrochloric acid used in inversion in the German method, in which 5 cc. is added to the solution to be inverted, the volume made up to 75 cc. and inverted by heating to 67° C. in fifteen minutes and cooled rapidly, after which the volume is increased to 100 cc. and the solution is polarized. The abscissas give the polariscopic readings of the solution of invert sugar in number of degrees to the left, and the ordinates give the increase in tenths of degrees that the addition of 5 cc. of hydrochloric acid causes.

Since the reading of the invert sugar before and after adding the hydrochloric acid was all that was needed in order to plot the diagram, two solutions of invert sugar were prepared: One by inversion with citric acid (2 grams to 100 cc.) and the other by use of N/5 sulphuric acid and the acid removed by the use of barium carbonate, which gives a solution of invert sugar free from any substances which might affect its optical action. Neither of these solutions was of a definite strength. Parallel experiments were carried on, using the two solutions; but the results as plotted in Fig. 1 were identical. The procedure in all of the following experiments was the same except for the varying amounts of hydro-

chloric acid added. Of the solution of invert sugar, 10, 15, and 50 cc. portions were measured into 100 cc. flasks, 5 cc. of hydrochloric acid (sp. gr. 1.20) were added to each in the cold and the solution was then made up to volume and polarized. For example, two 10 cc. portions were measured into 100 cc. flasks. To one, 5 cc. of hydrochloric acid were added, and the other was made up to volume and polarized at the same temperature. The one to which no acid had been added polarized  $-5.6^{\circ}$ , and that to which the acid had been added polarized  $-5.9^{\circ}$ , a difference of  $0.3^{\circ}$  which gives a point on the diagram. Another portion which polarized without acid  $-23^{\circ}$ , polarized  $-24.2^{\circ}$  with 5 cc. of hydrochloric acid, and a third portion which polarized  $-34.8^{\circ}$  without the addition of acid, polarized  $-36.7^{\circ}$  after its addition, an increase of  $1.9^{\circ}$  caused by the addition of the acid in the cold. These experiments show that with the same amount of acid the larger the invert reading the greater is the increase in the reading caused by the acid. Fig. 1 illustrates this point and from it one can easily determine in any particular case, as for instance, in polarizing a jam which reads  $-19.5^{\circ}$  before inversion and  $-20.5^{\circ}$  after inversion, that the change is not due to any sucrose present but is the change to be expected from the action of the acid. By examining the diagram it will be seen that 5 cc. of hydrochloric acid causes an increase of  $-1.05^{\circ}$  in reading in a solution that polarizes  $-19.5^{\circ}$  thus making the reading  $-20.55^{\circ}$ . Any one who has polarized honey to any extent has noticed this slight change. In Table III, I have noted a number of polarizations of honeys taken from U. S. Dept. of Agr., Div. of Chem., Bull. 13, and have corrected them from Fig. 2, which shows the effect of the amount of acid used in the method of the Association of Official Agricultural Chemists in which the larger amount of acid used (10 cc. in 110 cc., or nearly twice that used in the German method) causes a greater increase in the minus reading. The calculated minus readings are obtained by adding to the direct reading the correction for the effect of the acid as calculated from Fig. 2.

TABLE III.—POLARIZATION OF HONIES.

Direct.	Invert.	Degrees Ventske.	
		Cane sugar. <sup>1</sup>	Calculated invert reading.
— 20.00	— 20.90	0.72	— 21.25
— 17.60	— 18.32	0.93	— 18.59
— 16.8	— 18.40	1.23	— 18.20
— 15.8	— 17.5	1.31	— 16.78
— 11.0	— 12.0	...	— 11.68
— 13.2	— 15.6	...	— 14.00
— 16.50	— 18.00	...	— 17.52
— 14.80	— 15.60	...	— 15.70
— 9.40	— 10.67	0.96	— 9.98
— 12.90	— 13.86	0.73	— 13.70
— 14.40	— 15.40	0.76	— 15.39
— 11.30	— 12.65	0.99	— 12.00
— 11.50	— 12.65	0.85	— 12.21
— 13.50	— 14.00	0.30	— 14.33
— 9.5	— 10.00	0.30	— 10.05
— 11.0	— 12.00	0.70	— 11.68
— 10.0	— 11.00	0.70	— 10.62
— 11.0	— 12.00	0.70	— 11.68

Using the Herzfeld formula,<sup>2</sup>

$$S = \frac{a - b}{141.85 + 0.05b - \frac{T}{2}}$$

S = Sucrose.

a = Direct reading.

b = Invert reading.

T = Temperature,

in which 141.85, the factor for 1 gram of sucrose in 100 cc., is increased by 0.05 of the invert reading, and plotting a line in the same way as has been previously explained in plotting the results, it will be found that the two lines almost exactly coincide (see Fig. 1). For instance, suppose a minus polarization of —35° is multiplied by 0.05, giving 1.75°. As Herzfeld begins with a polarization of —1.3°, corresponding to 1 gram of sugar at 20°, we mark off on the line AB the point at which —1.3° would intersect it and draw A'D' and use that as a base line. At 35° on this base line measure 1.75° and it will be found to be almost exactly on

<sup>1</sup> As calculated from direct and invert reading.

<sup>2</sup> Herzfeld: *Ztschr. Rübensucker-Ind.*, 40, 194.

the line  $AB$ , which bears out the results previously obtained and shows that the method by which they were obtained is correct. In order to determine the effect caused by 10 cc. of hydrochloric acid in 110 cc. of sugar solution (the amount of acid used in the A. O. A. C. method), it is necessary to fix one point in Fig. 2 very carefully and from that to draw a straight line to the origin and there is obtained at once the correction to be made in the Herzfeld formula in order to obtain a new formula which will be correct for this method. In Fig. 2 is shown the determination of this correction. From Fig. 2 it is seen that the increase due to 10 cc. of hydrochloric acid (sp. gr. 1.20) in 110 cc. is 0.062 times the invert reading, while in the Herzfeld formula it was 0.050 times the invert reading. Therefore in order to make a formula for the official method, we substitute 0.062 for 0.050, also changing the factor 141.85, for 1 gram of sugar, to 141.79, which is apparently the limiting case if one plots the line. Thus we obtain the formula

$$S = \frac{a - b}{141.79 + 0.062b - \frac{T}{2}}$$

While this formula may be used for calculating the amount of sucrose present, for any concentration, from polarization before and after inversion, it does not, stated in this form, give a means for calculating small amounts of cane sugar in the presence of large amounts of invert sugar. In order to make this determination, a slightly different method of calculation must be pursued. As  $(0.062 \times b)$  is equal to the effect of the acid, if this is subtracted from  $b$ , it will give the true polarization, thus,

$$S = \frac{a - (b - (0.062 \times b))}{141.79 - \frac{T}{2}}$$

Now if  $a$  and  $(b - (0.062 \times b))$  are equal, it is evident that all the change in polarization has been due to the effect of the acid used in inversion on the invert sugar, while if there is still a difference the cane sugar can be calculated by the use of  $141.79 - \frac{T}{2}$ . This formula will not apply to fruit products containing glucose, but is of special value in estimating small amounts of cane sugar

in fruits, pure fruit jellies, jams, and honies in which large amounts of invert sugar are present.

The action of acid on invert sugar mixed with glucose is the same as it is on the same amount of invert sugar alone, as the following results show:

TABLE IV.

	Polarized. ° Ventske.	Temperature. °C.
13.028 grams invert sugar + 25 cc. glucose solution	+ 9.8	21.0
The same + 10 cc. hydrochloric acid.....	+ 8.9	21.0
The same + 5 cc. hydrochloric acid.....	+ 9.4	21.0

This shows that when glucose which contains invert sugar is polarized before and after inversion, there will be a change of polarization even if there is no sucrose present. This condition would be almost always found in honey adulterated with glucose. This obviously can not be corrected by the formula given, and the writer is working on the use of inverting agents, such as citric acid, which have practically no effect on the opticity of invert sugar.

These results show that if you eliminate the effect of the acid used in inversion, the *Clerget formula will become a constant for any given temperature regardless of the concentration of the sugar solution*. This can be seen by noting from Fig. 1 that the increase of invert reading caused by the hydrochloric acid is 0.05 of the invert reading, so that Herzfeld's formula would be

$$S = \frac{a - b}{141.85 - \frac{T}{2}}$$

if the effect of the acid was removed, or a constant at any temperature.

If an inverting agent could be obtained which had no effect on the invert sugar, the question of concentration would practically be eliminated. But the elimination of this error would necessitate the determination of a new factor which would in all probability be 141.79 or perhaps a little less.

From this work it will be seen that the smaller the amount of hydrochloric acid used, the less is the effect on the negative reading, and therefore the smaller the error due to concentration. It

will be seen from Table II that the effect of  $N/4$  hydrochloric acid is comparatively small, and the factor for any given temperature approaches a constant for all concentrations. All will agree that this is a most desirable condition for attaining accuracy.

The German method of using  $\frac{1}{2}$  normal weight (13.024 grams) and 5 cc. of hydrochloric acid reduces the error, as compared with the A. O. A. C. method, due to concentration, to a considerable extent, for two reasons. The smaller amount of acid has less effect on the negative reading and it has been shown from Table II that the smaller the amount of sugar used the less is the variation. As, for instance, the factor varies from 141.85 to 142.66, for 1 gram to 13 grams of sugar, a variation of  $0.81^\circ$ , and with the A. O. A. C. method it varies from 141.85 to 144.00,  $2.1^\circ$ .

The use of less acid for the inversion is desirable and it is in this direction that investigation should tend. The smaller the amount of the acid the less is the danger of destruction of the sugar and the smaller the error due to concentration, but it must be remembered that every change in the strength or amount of acid used requires the most careful determination of a new factor.

The work can be summed up in this way:

1. Hydrochloric acid increases levo-rotation of an invert sugar solution.
  2. This increase, other things being equal, is proportional to the quantity of hydrochloric acid used.
  3. Other things being equal and temperature varying, hydrochloric acid increases levo-rotation by a definite per cent. of the polarization.
  4. In order to correctly calculate the percentage of cane sugar in invert sugar by Clerget's formula a correction depending on the amount of hydrochloric acid used must be made, which can be calculated from Fig. 1 or 2. All readings of the polariscope should be made at or about  $20^\circ$ .
-



## THE SUBSTITUTION OF HYDROGEN FOR CHLORINE IN TRICHLORMETHYLPARACONIC ACID.

(SECOND PAPER.)

BY HENRY C. MYERS.

Received February 22, 1902.

IN the *Journal of the Chemical Society* for June, 1897, I called attention to some extremely unstable condensation products resulting from the reduction of dichlormethylparaconic acid in attempting to eliminate the remaining chlorine atoms. One compound being monochlordiparaconic acid,  $C_8H_6ClO_2$ , and another, also an acid, having the formula  $C_8H_{12}O_2$ . Secondary to other published work, I have continued these investigations.

Finding that the reduction of the dichlor acid by various agents was not in the direction of methylparaconic acid, which substance I hoped to reach by this method, I decided to treat the trichlor acid with sodium amalgam, the trichlor acid being readily prepared on condensation of chloral with sodium succinate in the presence of a suitable dehydrating agent.<sup>1</sup>

Trichlormethylparaconic acid was dissolved in water, treated with sodium hydroxide to retard the action of free acid, small pieces of solid sodium amalgam added occasionally and the cylinder surrounded with ice. Frequently during a two-days' treatment, sulphuric acid was added to prevent the solution becoming more than weakly alkaline. Eventually sulphuric acid was added in large excess and the mixture extracted with ether; on recrystallization from water the result was found to be an almost quantitative yield of the dichlor acid. This method, as regards the preparation of dichlormethylparaconic acid, is much simpler than the laborious process of reducing with zinc dust and acetic acid and finally precipitating with hydrogen sulphide as described by Miller (*Loc. cit.*), large amounts of zinc being precipitated completely only on repeated treatment with hydrogen sulphide, and filtration being extremely slow and unsatisfactory.

<sup>1</sup> Miller: *Ber. d. chem. Ges.*, 23, R. 92 (1890); *Ann. Chem.* (Liebig), 288, 43.

## LONG-CONTINUED REDUCTION.

The above treatment with sodium amalgam when continued for a week or ten days resulted in three definite compounds, one of which has never been previously observed; (a) the dichlor acid with its characteristic properties and melting-point of  $142^{\circ}$ ; (b) monochlordiparaconic acid of orange color and melting-point of  $220^{\circ}$ , obtained by recrystallization from alcohol; (c) a new acid in relatively small amounts with melting-point of  $126^{\circ}$ - $127^{\circ}$  and found in the final ether extraction as follows: On completion of the treatment with sodium amalgam the solution was acidified with hydrochloric acid. The monochlordiparaconic acid being insoluble in water formed an extremely voluminous precipitate which was filtered off and recrystallized from alcohol. The filtrate on extraction with ether yields the white crystalline dichlor acid, readily purified by crystallization from water. Repeated extraction with ether gives a yellowish oil which on long standing over sulphuric acid forms well defined crystals. These on being recrystallized from water and washed with ether have a constant melting-point of  $126^{\circ}$ - $127^{\circ}$ , resemble benzoic acid in appearance, do not decompose on standing for a year, are soluble in sodium carbonate solution, acid to litmus, and do not decompose on repeated melting.

## BEHAVIOR OF MONOCHLORDIPARACONIC ACID TOWARDS HEAT.

In making melting-point determinations of this acid in the usual way, with capillary tube and paraffin-bath, it was noticed that the acid on melting underwent decomposition giving off a gas in small bubbles. In order to observe the change more closely, a long slender test-tube was substituted and considerable material used. In this way it could be observed that the substance really began its decomposition at about  $190^{\circ}$ , giving off fumes of hydrochloric acid and depositing white needle-like crystals on the tube just above the paraffin. I doubt if the true conditions of melting-points so called, can be observed in minute capillary tubes. These observations resulted in my placing about 3 grams of material in a U-tube heating the same as high as  $226^{\circ}$ , meanwhile drawing air through the apparatus. The air was previously freed of moisture and carbon dioxide; the products of the change were drawn

through calcium chloride, silver nitrate and caustic potash. Sublimation began at  $181^{\circ}$  followed by an effervescence of gas at  $190^{\circ}$ . The following figures show the total loss in weight in the U-tube and the corresponding increase in weight in each of the receiving tubes:

	Gram.
Loss in U-tube.....	0.6097
Gain in calcium chloride tube.....	0.0369
Gain in caustic potash tube.....	0.0662
Gain in silver nitrate tube.....	0.4854

CALCULATED LOSS CORRESPONDING TO 1 MOLECULE OF EACH GAS USING  
2.9470 GRAMS OF MATERIAL.

	Calculated.	Found.
Hydrochloric acid gas.....	0.5830	0.4854
Water .....	0.2875	0.0369
Carbon dioxide.....	0.7028	0.0662
		<hr/> 0.5885

As the weights of water and carbon dioxide are too low for the loss of a single molecule and the total gain corresponds almost exactly with the loss of a single molecule of hydrochloric acid (calculated 0.5830, found 0.5885) I assume that the change is represented by the following reaction:



and that the increase in weight in the calcium chloride and caustic potash tubes were due to hydrochloric acid alone.

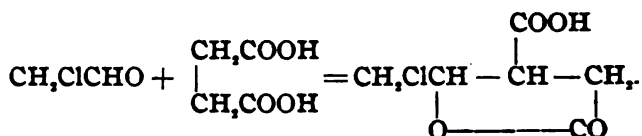
CONCLUSION.

Trichlormethylparaconic acid on reduction with either zinc dust or sodium amalgam in the presence of acids produces the dichlor acid in almost quantitative amounts, except where treatment is long continued with the amalgam. In the latter case, three distinct and well defined acids result; viz., Dichlormethylparaconic acid, monochloridiparaconic acid, and a new acid with melting-point at  $126^{\circ}$ - $127^{\circ}$ . The dichlor acid on reduction produces monochloridiparaconic acid, according to the following equation:<sup>1</sup>



<sup>1</sup> *J. Chem. Soc.*, June, 1897.

Monochlordiparaconic acid on reduction forms an acid,  $C_5H_{12}O_5$ , which I found too unstable for investigation. Considering that these reductions do not lead in the direction of methylparaconic acid and that aldehyde as well as chloral condenses with sodium succinate in the presence of dehydrating agents, it would be of interest to treat similarly the monochlor aldehyde. Possibly the following change might result:



This monochlormethylparaconic acid, which I believe has never been prepared, might reduce to methylparaconic acid and yet the tendency of these compounds seems to be to double the molecular weight on giving up chlorine. On account of the extreme complexity of these changes and the instability of resulting compounds, as well as the great length of time necessary to prepare material, very little progress can be made unless one is willing to devote a year to the question as it now stands.

UNIVERSITY OF CALIFORNIA.

---

[CONTRIBUTION FROM THE NORTH CAROLINA EXPERIMENT STATION.]  
**NITRIFICATION IN DIFFERENT SOILS.<sup>1</sup>**

BY W. A. WITHERS AND G. S. FRAPS.

Received February 22, 1902.

IN a previous article<sup>2</sup> the authors communicated some work on the rate of nitrification of some fertilizers in a pasture soil, in which it was found that the percentages of nitrogen in them nitrified in a definite time corresponded with their availability as measured by vegetation tests, with one exception. This exception was ammonium sulphate, which was nitrified to a very small extent, although it has a high availability.

Inasmuch as the prevailing opinion in regard to the process of nitrification is that organic nitrogen is first converted into am-

<sup>1</sup> An account of this work was read before the Association of Official Agricultural Chemists in November, 1901.

<sup>2</sup> This Journal, 23, 318 (1901).

monium salts, then into nitrites, then to nitrates, it seemed strange that ammonium sulphate should possess a low rate of nitrification. Results of experiments by other workers were cited, in one of which ammonium sulphate was nitrified to a greater extent than dried blood, in the other to a less extent.

The explanation we then put forward to account for the unexpected behavior of ammonium sulphate is as follows:

1. Ammonium sulphate may hinder the action of the nitrifying organisms. This explanation does not account for the beneficial action of calcium carbonate.

2. The nitric and sulphuric acids formed by the action of the nitrifying organisms are detrimental to them, being neutralized only in part by the bases of the soil. This does not explain why a soil should nitrify dried blood more rapidly than ammonium sulphate, even when calcium carbonate is added.

3. Different soils contain different nitrifying organisms, some of which convert organic matter directly to nitrites, while others change ammonium salts to nitrites more readily.

All three of the above causes may be in operation. The work to be described is a continuation of that mentioned above, and was designed to test the hypotheses then put forward.

#### PLAN OF WORK.

The work was confined to a study of the comparative rate of nitrification of ammonium sulphate and cottonseed meal in different soils, both with and without the addition of calcium carbonate. The soils were obtained from different sections of the country and varied widely in their composition and properties.

The procedure was that described in the paper already referred to. The sample of soil was sifted through a coarse sieve, and the quantity of cottonseed meal or ammonium sulphate, containing 0.3 gram nitrogen, was intimately mixed with 500 grams of it. In some cases, additional tests were made with half this quantity of nitrogen. The mixture was placed in precipitating jars, and kept in a dark closet. When calcium carbonate was added, the amount taken was exactly sufficient to neutralize all the nitric and sulphuric acids which would be produced if the ammonium sulphate were completely nitrified. The same quantity was used for the cottonseed

meal. The amount of water in the soils was about 15 per cent.: at suitable periods, one or more jars in each set was weighed, and the estimated loss of moisture was replaced in all the jars. At the end of three weeks (a little longer in some cases), the nitrates were leached out, and determined by the Tiemann-Schulze method, correction being made for the nitrates formed in the soil to which no fertilizer had been added.

#### DESCRIPTION OF SOILS.

1667. Pasture soil from the farm of this college. A light loam, containing humus and not acid to litmus.

1668. Heavy clay soil from college farm. Contains very little humus, possesses low fertility, and is slightly acid to litmus.

1669. Black garden soil from Florida Experiment Station. Contains much humus and is acid to litmus.

1670. Soil from the Massachusetts Hatch Experiment Station. This soil is from a plot in field C, fertilized with ammonium sulphate, muriate of potash, dissolved bone-black, and stable manure since 1891. This is the plot giving the least satisfactory growth, especially upon lettuce, beets, spinach and onions. It contained little humus and was acid to litmus.

1674. Soil from Rhode Island Experiment Station, used in plot experiments. Slightly acid to litmus, contains humus.

1675. Sandy soil from the Red Springs test farm of the North Carolina Department of Agriculture. Contains little humus.

1676. Soil from plot 23, Rhode Island Experiment Station, fertilized with ammonium sulphate. This soil, and also 1677, 1678, and 1679, is from a series of plots which have been in use for some time to test the effect of lime on an acid upland soil.

1677. Soil from plot 25, fertilized with ammonium sulphate and lime.

1678. Soil from plot 27, fertilized with sodium nitrate.

1679. Soil from plot 29, fertilized with sodium nitrate and lime.

1680. Sandy soil from Tarboro test farm of the North Carolina Department of Agriculture.

Acknowledgment is hereby made to Director H. J. Wheeler, of Rhode Island, Chemist H. K. Miller, of Florida, Agriculturalist W. P. Brooks, of Massachusetts, and State Chemist B. W. Kil-

gore, of North Carolina, for their kindness in furnishing samples of soil.

## EXTENT OF NITRIFICATION.

The table contains the result of the nitrification tests, expressed in percentage of the total nitrogen nitrified. It also gives the temperature and the water content of the soils.

Tests were made, with lead acetate paper, to see if any hydrogen sulphide was evolved during the nitrification. The soil extract was also examined. The results were negative.

## NITRIFICATION IN SOILS.

	Average moisture. Per cent.	Temperature.		Per cent. nitrified.	
		Extremes. °C	Mean. °C.	Alone.	With CaCO <sub>3</sub> .
1667. Ammonium sulphate ....	10.5	25-30	27	7.2	57.2
Cottonseed meal.....	...	...	..	32.4	43.6
½ ammonium sulphate..	...	...	..	...	71.8
½ cottonseed meal.....	...	...	..	...	43.0
Ammonium sulphate and cottonseed meal.....	...	...	...	...	22.3
1668. Ammonium sulphate ....	13.0	25-30	27	0.6	11.6
Cottonseed meal.....	...	...	..	0.0	-1.1
½ ammonium sulphate ..	...	...	..	...	43.2
1669. Ammonium sulphate ....	13.0	25-30	27	0.2	15.8
Cottonseed meal.....	...	...	..	17.3	41.5
1670. Ammonium sulphate ....	15.0	23-28	26	2.2	45.7
Cottonseed meal.....	...	...	..	14.8	32.6
Ammonium sulphate and cottonseed meal.....	...	...	..	0.5	...
1674. Ammonium sulphate ....	10.7	20-26	22	2.1	2.3
Cottonseed meal.....	...	...	..	3.4	4.9
½ ammonium sulphate..	...	...	..	...	16.5
½ cottonseed meal.....	...	...	..	...	10.9
Ammonium sulphate and cottonseed meal.....	...	...	..	1.3	...
1675. Ammonium sulphate ....	8.0	19-24	20	0.0	0.0
Cottonseed meal.....	...	...	..	0.0	0.0
1676. Ammonium sulphate ....	12.2	18-23	19	0.0	1.5
Cottonseed meal.....	...	...	..	1.9	-1.3
½ ammonium sulphate..	...	...	..	..	1.5
½ cottonseed meal.....	...	...	..	..	0.6

	Average moisture. Per cent.	Temperature.		Per cent. nitrified.	
		Extremes. °C.	Mean. °C.	Alone.	With CaCO <sub>3</sub>
1677. Ammonium sulphate ....	11.7	18-23	19	1.0	5.6
Cottonseed meal.....	...	...	..	1.8	6.2
1678. Ammonium sulphate ....	12.1	18-23	19	0.0	0.6
Cottonseed meal.....	...	...	..	0.0	0.0
1679. Ammonium sulphate ....	12.5	18-23	19	1.2	3.0
Cottonseed meal.....	...	...	..	2.9	10.6
1680. Ammonium sulphate ....	9.5	19-24	20	0.0	-1.3
Cottonseed meal.....	...	...	..	1.3	-0.8
½ ammonium sulphate ..	...	...	..	..	0.8
½ cottonseed meal .....	...	...	..	..	4.5

## DISCUSSION OF RESULTS.

*Effect of Temperature.*—The nitrification was much more active in the first four soils, in which the temperature was 23°-30° C., than in the others, in which the temperature was lower.

*Effect of Calcium Carbonate.*—The addition of calcium carbonate invariably caused increased nitrification, if any nitrification at all took place. For example, the increase was from 100 to 366, 100 to 240 with cottonseed meal, and 100 to 800, 100 to 2100 with ammonium sulphate. In some soils, nitrification did not occur when calcium carbonate was not added. Previous liming of the soil did not keep the calcium carbonate from being effective.

*Effect of Previous Liming of the Soil.*—Practically no nitrification occurred in the acid unlimed soils (1676 and 1678), even in presence of calcium carbonate, while the same soil previously limed (1677 and 1679) nitrified the fertilizers.

*Effect of Previous Fertilizers.*—A limed soil (1677) fertilized with ammonium sulphate for some years nitrifies ammonium sulphate much more readily than the same soil which had received sodium nitrate (1679).

*Variation in the Nitrifying Power of Soils.*—All our results on different soils are not comparable, since the nitrification did not all take place at the same temperature. But we can easily see, that while some soils nitrify ammonium sulphate to a greater extent in three weeks than cottonseed meal, there are others in which the reverse is the case.



*Effect of Increasing Ration of Soil to Fertiliser.*—This usually resulted in a slight increase in the quantity of nitrates formed, thus involving a very great increase in the percentage of nitrification.

#### EXPLANATION OF RESULTS.

We will now discuss the bearing of these results upon the explanations we have previously put forward.

1. Ammonium sulphate may hinder the action of the nitrifying organisms. Additional evidence in favor of this hypothesis is afforded by the fact that the process of nitrification is more rapid when the quantity of ammonium sulphate is reduced.

2. Detrimental action of the nitric and sulphuric acids. This is in accord with the fact that calcium carbonate was always beneficial. This explanation has been generally accepted for a long time.

3. Different soils contain different organisms. This is in accord with our observation that some soils nitrify ammonium sulphate more rapidly than cottonseed meal, and with others the reverse is true. This is exactly what was expected when the experiments were instituted.

#### THE NITRIFYING ORGANISMS.

Our third hypothesis seems to be in opposition to the prevailing opinion that organic matter must necessarily be converted into ammonia as the first stage in nitrification. It does not seem to be in opposition to the facts as recorded in the literature on this subject, however, so far as we have been able to find. Warington, Frankland, and Stutzer each found that the pure nitrous organism is capable of nitrifying organic nitrogen. Omelianski<sup>1</sup> disputes this, and says that pure cultures of nitrifying bacteria are incapable of nitrifying organic nitrogen, but it must be converted into ammonia first. He claims that the opposite conclusions reached by Frankland, Warington, and Stutzer and his associates were based upon inaccurate observations. But it is possible that the organisms are different.

But even if it is true that Omelianski is right, it does not neces-

<sup>1</sup> Experiment Station Record, 12, 115 (1901), aba

sarily follow that bacteria which nitrify organic nitrogen to nitrites do not exist. All the conditions under which the nitrous organisms have been isolated tend to eliminate such germs, the cultures always taking place in the presence of ammonium salts as a source of nitrogen, and organic nitrogen being excluded. Such a medium is unfavorable to the nitrate bacterium, also. The isolation of the bacteria which oxidize organic nitrogen must be conducted in a medium containing organic nitrogen, but not gelatine, since it has been found heretofore that species of bacteria separated by culture on gelatine do not nitrify at all.

#### SUMMARY.

1. Addition of calcium carbonate invariably accelerates the nitrification of cottonseed meal and ammonium sulphate, especially the latter.
  2. In some soils a greater percentage of the nitrogen in ammonium sulphate is nitrified than that in cottonseed meal, and in other soils, the contrary is the case, even in the presence of calcium carbonate.
  3. The factors which produce this result are probably as follows: *a.* The presence of the ammonium sulphate diminishes the activity of the nitrifying organisms; *b.* The acids produced also hinder them; *c.* Different soils contain different classes of organisms, some of which nitrify organic in preference to ammoniacal nitrogen.
  4. We have found no evidence on record that organisms which nitrify organic nitrogen directly do not exist. The fact that they have not been isolated by present methods may be due to their elimination by the use of ammonium salts, on which they cannot feed, in the nutritive medium.
  5. Liming acid soils is favorable to nitrification.
  6. Continuous application of ammonium sulphate to a soil previously limed increases its power of nitrifying ammonium sulphate.
-

## NEW APPARATUS IN WATER ANALYSIS.

BY GEORGE EDWARD THOMAS AND CLARENCE A. HALL.

Received March 12, 1902.

It is the purpose of the writers of this paper to present some new forms of apparatus which have been devised for use in the Chemical Laboratory of the Filtration Testing Station in connection with the improvement of the water supply of the City of Philadelphia.

### I.

The first apparatus described is used in the determination of the free and albuminoid ammonia, according to the method of Wanklyn, consisting of a battery of six stills as shown in Fig. 1.

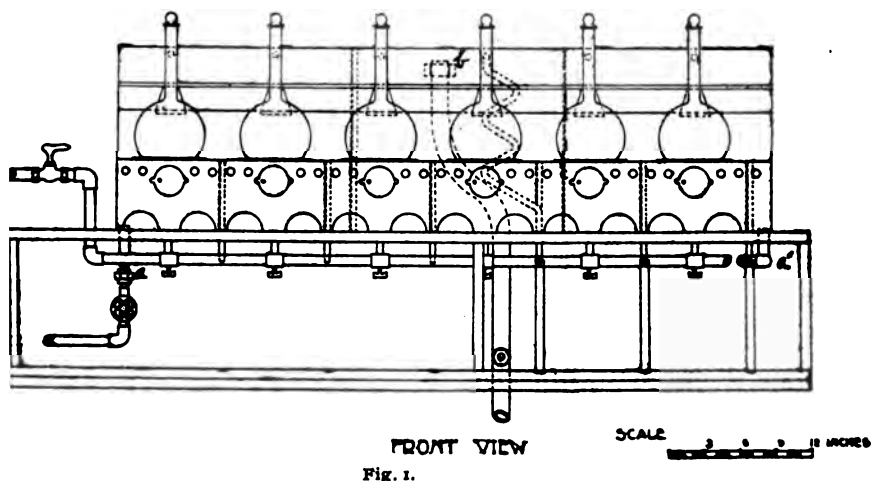


Fig. 1.

The flasks have side necks and ground glass stoppers, the capacity of the bulb being about 1800 cc. They are supported upon a burner shield constructed of galvanized sheet iron, the flasks resting upon wire gauze in holes  $4\frac{3}{8}$  inches in diameter. The burners are of a modified Fletcher type and are governed by individual cocks and a valve connected with the general supply. The flasks are united with the block tin worms by the side necks, which

are provided with rubber tubing—and extend into the tubes some distance beyond the point of contact of the rubber with the block tin (see Fig. 2), another piece of tubing overlapping this joint making a tight connection. The worms are  $\frac{3}{8}$  inch internal and  $\frac{1}{2}$  inch external diameter, coiled in a helix  $2\frac{1}{2}$  inch internal diameter with a  $4\frac{1}{2}$  inch pitch, being expanded at the entrance to

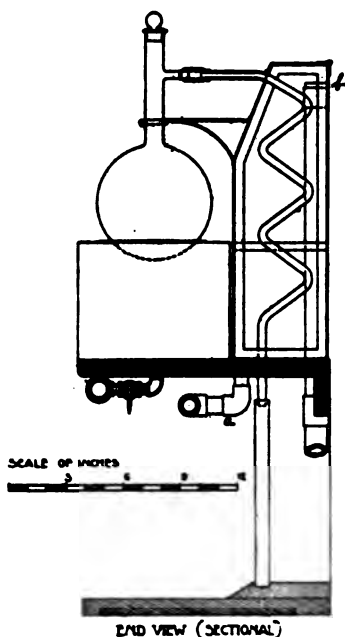


Fig. 2.

allow for the connection with the side necks of the flasks, and contracted for 1 inch at the outlets. The condenser is made of cold rolled sheet copper, 24 oz. per square foot, braced on the inside and provided with a lid hinged at the back and overlapping the front. The water is supplied at the extreme ends *a* and *a'* and overflows at the top *b* thus insuring thorough circulation. The whole system is supported upon a wooden shelf, allowing the operator ample space for handling the distillates, the Nessler tubes resting in sockets on a wooden slab upon the table. The salient features of this apparatus appear in its compactness, the manner

of connecting the flasks with the tin condensing worms, and the ground glass stoppers avoiding disconnection with the condensing tubes for the introduction of the alkaline permanganate prior to liberating the albuminoid ammonia.

Before making a determination, the system is cleansed by boiling off 50 cc. of distillate from 500 cc. of pure water rendered alkaline with sodium carbonate. 500 cc. of the sample are introduced and the determination made in the usual manner.

## II.

The second apparatus to which attention is directed is shown in Fig. 3 and is used in collecting samples from reservoirs or rivers

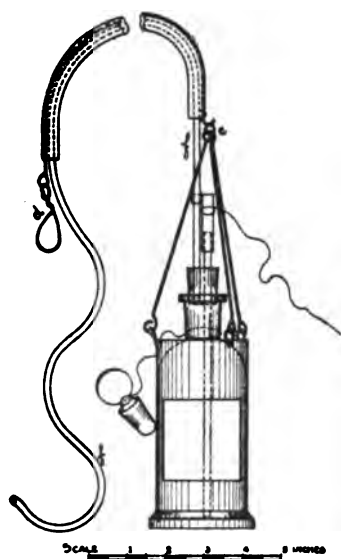


Fig. 3.

for the determination of the dissolved oxygen or carbon dioxide. It comprises a copper case, weighted at the base with sheet lead, holding securely a calibrated bottle of about 250 cc. capacity. This is supported by three copper wires joined at *c* and is suspended by the copper wire *d*. A glass tube passes through one of the holes of the rubber stopper nearly to the bottom of the bottle for the inlet of water; through the other a tube passes for the exit

of air; the former is supplied with a cap and the latter with rubber tubing which reaches to the surface. The wire *d* and the rubber tubing are surrounded by a  $\frac{1}{4}$  inch rubber tube to prevent them from becoming entangled while the sample is being collected. The bottle is lowered until the required depth is reached, when the cap is removed by means of the string attached, allowing the water to enter. The apparatus is kept submerged until air is no longer expelled from the tube *f*, then the sample is raised to the surface, the wires disconnected and the rubber stopper removed, allowing the water remaining in the rubber tube *f* to fill the bottle to overflowing. The glass stopper attached is then inserted, the bottle taken from the case, the sample being ready for analysis.

### III.

In the third division of our paper, a method is described for the determination of suspended matter. After an exhaustive study of various methods employed, we have found that the most satisfactory results can be obtained by filtering the water through asbestos.

Long fiber asbestos is soaked several days in a large quantity of clear (not distilled) water, which is frequently decanted and fresh portions are added. At the bottom of a Royal Meissen Gooch crucible, a layer of 3 mm. gravel is spread, this having been previously washed. A small quantity of asbestos is next placed on the gravel; it is necessary to separate the fibers by suspending it in water, as a good filter cannot be made by using a compact mass. After adding the asbestos, the crucible is placed to the lips and the bulk of the water held by the fibers blown out. There should now remain a perfect mat of asbestos covering the gravel and upon this the filter proper is constructed. More fiber is now added, in small portions, tapping the crucible lightly after each addition. When it is filled the forefinger is used to mold the asbestos around the sides of the crucible. The major portion of the water is now expelled by blowing, when the entire inner surface of the crucible should be covered with a compact asbestos lining. Any imperfections found in this surface necessitates reconstruction.

A perforated porcelain thimble is placed inside of the partially formed filter and more asbestos packed around the intervening space, nearly filling the crucible (see Fig. 4). Then the filter is

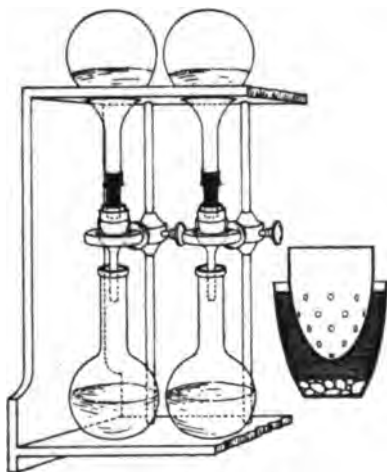


Fig. 4.

ready to be dried and weighed; it is necessary to heat for five hours at  $110^{\circ}\text{C.}$ , in order to remove all the moisture, after which it is cooled in a desiccator and weighed rapidly, for the dissolved solids remaining in the filter may render it hygroscopic.

The method is to place the tared filter in the rack as indicated in the drawing, and to supply from a liter flask 1000 cc. of the sample of water for the determination. Loss is prevented while inverting the flask by compressing the rubber tubing at the neck, and by making use of the principle of the pneumatic trough the sample is fed automatically, part of the filtrate being used to wash down the particles adhering to the sides of the flask, again inverting and collecting the same upon the filter.

The crucible containing the suspended matter is dried and weighed under the same conditions as when prepared for use, the difference in weight representing the solid matter in suspension. In working with water carrying an unknown amount of dissolved solids the filter is first washed with some of that water and tared. This form of filter may be used repeatedly before it becomes inefficient, and it has been found convenient to use a battery of six units.

[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY,  
No. 62.]

## AROMATIC BASES AS PRECIPITANTS FOR RARE EARTH METALS.<sup>1</sup>

BY ALICE MACMICHAEL JEFFERSON.

Received February 22, 1902.

THE purpose of the present investigation was to ascertain to what degree certain well-defined aromatic bases might be applied in metal precipitations.

It seemed advisable to restrict this study to the rare earth metals. To this end salts of zirconium, thorium, cerium, lanthanum, neodymium and praseodymium were selected, and these were acted upon in succession by the bases—aniline, *o*-toluidine, xyloidine, dimethyl aniline, diethyl aniline, benzylamine, pyridine, piperidine, quinoline and phenyl hydrazine. Knowing the action of the mother base—ammonia—it was of interest to discover to what degree substituted ammonias and kindred bodies might affect the salts chosen for the study. The hope was also cherished that if differences in behavior with the proposed reagents were disclosed, perhaps separations of some of the metals might possibly be realized. It will be generally admitted that the probability of discovering such results would truly warrant a study such as has been indicated in the preceding lines.

### I. ZIRCONIUM.

Solutions of zirconium nitrates were prepared with great care and used in the experiments about to be described.

*Zirconium and Aniline.*—A definite amount of the zirconium salt solution was removed by means of a pipette, and diluted to about 50 cc. To this, aniline was added and the liquid thoroughly agitated. A beautiful white, gelatinous precipitate separated almost immediately. It was allowed to stand over night and in the morning it was filtered, washed, dried, ignited and weighed. The results indicate that the reaction took place quantitatively.

<sup>1</sup> From author's thesis for Ph.D., 1901.



	Salt taken.	ZrO <sub>2</sub> found.	Required.	Found.
	Gram.	Gram.	Per cent.	Per cent.
I.	0.1382	0.0738	39.13	39.36
II.	0.0841	0.0436	39.13	38.24
III.	0.1050	0.0486	34.13	34.13
IV.	0.0908	0.0399	32.27	32.38
V.	0.3479	0.1248	26.45	26.46

Throughout the work the zirconium dioxide was ignited with a blast-lamp to constant weight.

*Zirconium and o-Toluidine.*—*o*-Toluidine also reacted quantitatively, giving a white gelatinous precipitate very similar to that obtained with xylidine. It was allowed to stand twelve hours before filtering.

	Salt taken.	ZrO <sub>2</sub> found.	Required.	Found.
	Gram.	Gram.	Per cent.	Per cent.
I.	0.15084	0.0463	22.90	22.64
II.	0.15084	0.0463	22.90	22.64

*Zirconium and Xylidine.*—Xylidine precipitated zirconium quantitatively from its salts. About 50 cc. of the same solution were placed in a small beaker and xylidine added drop by drop with constant stirring. A white gelatinous precipitate formed which remained in suspension for some time. After twelve hours it was filtered, ignited, washed and weighed as zirconium dioxide. The precipitate was filtered with comparative readiness.

	Salt taken.	ZrO <sub>2</sub> found.	Required.	Found.
	Gram.	Gram.	Per cent.	Per cent.
I.	0.0908	0.0397	32.27	32.25
II.	0.0908	0.0401	32.27	32.58
III.	0.3479	0.1245	26.45	26.39

*Zirconium and Dimethyl Aniline.*—Dimethyl aniline was added to a portion of the zirconium solution with constant stirring. A yellowish white precipitate began to form slowly, and increased upon standing. After it had stood twelve hours it was filtered, washed, ignited to constant weight and the results calculated. It was found advisable to use a filter-pump in order to minimize the time factor for the excess of the precipitant filtered very slowly. The filtrate had a pink tinge.

	Salt taken. Gram.	ZrO <sub>2</sub> found. Gram.	Required. Per cent.	Found. Per cent.
I.	0.0908	0.0394	32.27	32.00
II.	0.3479	0.1248	26.45	26.46

*Zirconium and Diethyl Aniline.*—The precipitation was made exactly as with dimethyl aniline. The products were very similar in appearance. The reaction took place rather slowly, and it was found advantageous to stir the liquid from time to time. After twelve hours it was filtered using a suction-pump and at times a slight violet tinge was noticed in the filtrate.

	Salt taken. Gram.	ZrO <sub>2</sub> found. Gram.	Required. Per cent.	Found. Per cent.
I.	0.1050	0.0494	34.13	34.65
II.	0.0908	0.0401	32.27	32.58
III.	0.3479	0.1251	26.45	26.52

*Zirconium and Benzylamine.*—Benzylamine precipitated zirconium solutions quantitatively. The mass separated in small white floccules, which after standing a short time were easily filtered, and finally estimated as zirconium dioxide.

	Salt taken. Gram.	ZrO <sub>2</sub> found. Gram.	Required. Per cent.	Found. Per cent.
I.	0.2158	0.0863	29.68	29.50

*Zirconium and Pyridine.*—A definite amount of the zirconium solution was placed in a small beaker, diluted to about 50 cc., and pyridine added with constant stirring. A very beautiful white glistening precipitate formed which settled rapidly and filtered readily after standing about an hour. After washing it was allowed to dry, and finally ignited with a blast lamp to constant weight. The results were as follows:

	Salt taken. Gram.	ZrO <sub>2</sub> found. Gram.	Required. Per cent.	Found. Per cent.
I.	0.0841	0.0438	39.13	38.41
II.	0.1050	0.0490	34.13	34.36
III.	0.1050	0.0486	34.13	34.13
IV.	0.0908	0.0399	32.27	32.38
V.	0.1814	0.0743	30.17	30.21

*Zirconium and Piperidine.*—Piperidine also seemed to precipitate zirconium solutions quantitatively. The precipitate formed almost immediately upon agitation, and was gelatinous and beautifully white in color. As soon as it had settled it was filtered and ultimately weighed as zirconium dioxide, after being ignited with a blast-lamp to constant weight.

	Salt taken. Gram.	ZrO <sub>2</sub> found. Gram.	Required. Per cent.	Found. Per cent.
I.	0.0691	0.0367	39.13	39.18
II.	0.1050	0.0497	34.13	34.90
III.	0.0908	0.0404	32.27	32.82
IV.	0.2436	0.0876	26.45	26.52
V.	0.3479	0.1245	26.45	26.39

*Zirconium and Quinoline.*—When the zirconium salt was treated with quinoline and thoroughly stirred, a white glistening rather flocculent precipitate formed, which remained suspended for some time intermingled with the excess of the precipitant without settling. It was allowed to stand over night, then was filtered and ignited as before. In this case also the results seemed to indicate that a quantitative reaction had taken place.

	Salt taken. Gram.	ZrO <sub>2</sub> found. Gram.	Required. Per cent.	Found. Per cent.
I.	0.0841	0.0452	39.13	39.60
II.	0.1050	0.0497	34.13	34.90
III.	0.1508	0.0463	22.90	22.64
IV.	0.1508	0.0462	22.90	22.59

The action of diphenylamine—a very weak base—upon zirconium salts was not tried, and it was found that phenyl-hydrazine caused no precipitation in such solutions.

It will be observed that nine of the ten precipitants were basic enough to remove zirconium from its salts. None of the substituted anilines proved too feeble for this purpose, notwithstanding the presence in them of positive groups.

## II. THORIUM.

Here as with zirconium it was found that a solution of the nitrate was best adapted for the work. It was accordingly prepared by several methods and carefully tested as to its purity.

*Thorium and Aniline.*—Aniline precipitates thorium salts quantitatively. The precipitate did not form at once, but after the solution had stood a short time a cloudiness appeared in the solution and gradually increased. The precipitate was always allowed to stand over night, and if by that time it had not separated out nicely after stirring, it was allowed to stand another twelve hours. The clear white gelatinous mass was then filtered, and ultimately determined as thorium dioxide. The results were as follows:

	Salt taken. Gram.	ThO <sub>2</sub> found. Gram.	Required. Per cent.	Found. Per cent.
I.	0.1354	0.0651	42.29	42.25
II.	0.1354	0.0662	42.29	42.96
III.	0.1083	0.0519	42.29	42.11
IV.	0.1605	0.0768	42.29	42.05

*Thorium and o-Toluidine.*—o-Toluidine, like the other reagents, at first gave no precipitate, but on standing a heavy white very gelatinous mass formed. After several days, when the precipitate appeared to have settled nicely, the liquid was filtered and the precipitate was ignited and weighed. The resulting thorium dioxide after heating to constant weight with a blast-lamp, gave the following percentages:

	Salt taken. Gram.	ThO <sub>2</sub> found. Gram.	Required. Per cent.	Found. Per cent.
I.	0.1212	0.0577	42.29	41.81
II.	0.3210	0.1535	42.29	42.02
III.	0.3318	0.1582	42.29	41.85

*Thorium and Xylidine.*—Xylidine with thorium salts also gave a heavy white gelatinous precipitate. The solution was diluted to not more than 50-75 cc. and xylidine added with constant stirring. The precipitate remained with the excess of the precipitant, but after standing several days it settled upon the bottom of the beaker, and was estimated as usual.

	Salt taken. Gram.	ThO <sub>2</sub> found. Gram.	Required. Per cent.	Found. Per cent.
I.	0.0541	0.0257	42.29	41.69
II.	0.1134	0.0537	42.29	41.60
III.	0.1605	0.0774	42.29	42.37
IV.	0.1605	0.0758	42.29	42.05

*Thorium and Dimethyl Aniline.*—Considerable time elapsed before any precipitate formed. After several days no reaction seemed to have taken place, but at the expiration of a week or ten days a precipitate was noticed which was filtered and its quantity determined. When the reaction commenced the solution seemed to separate into two layers, one whitish and opaque, and the excess of the dimethyl aniline, being lighter in specific gravity, remaining on top. On stirring, however, a white, very gelatinous precipitate formed, which filtered very slowly, one drop at a time; therefore a suction pump was found to facilitate the reaction considerably. The results are as follows:

	Salt taken. Gram.	ThO <sub>2</sub> found. Gram.	Required. Per cent.	Found. Per cent.
I.	0.1605	0.0774	42.29	42.37
II.	0.1605	0.0777	42.29	42.54

*Thorium and Diethyl Aniline.*—Diethyl aniline seemed to react quantitatively with thorium salts, but the desired result was reached with difficulty. At first no precipitation took place. After standing some time a yellowish white voluminous precipitate separated out. The product seemed more or less dependent upon conditions such as temperature, concentration, etc. The most satisfactory results were obtained from 25-50 cc. of solution, and when the beaker was permitted to stand in a rather warm place. Usually no precipitate formed until the solution had stood several days, and for one determination it stood one whole week before filtering. The mass was extremely gelatinous and at times almost transparent. The results were:

	Salt taken. Gram.	ThO <sub>2</sub> found. Gram.	Required. Per cent.	Found. Per cent.
I.	0.1624	0.0796	42.29	43.05
II.	0.1083	0.0517	42.29	41.92
III.	0.1512	0.0725	42.29	42.11
IV.	0.1605	0.0761	42.29	41.66
V.	0.3318	0.1579	42.29	41.82

*Thorium and Pyridine.*—When pyridine was added to the thorium salt, for a few minutes no reaction took place, but after

standing a white gelatinous mass separated out, slightly less dense than that obtained with piperidine.

	Salt taken. Gram.	ThO <sub>2</sub> found. Gram.	Required. Per cent.	Found. Per cent.
I.	0.1083	0.0525	42.29	42.57
II.	0.1512	0.0737	42.29	42.81
III.	0.0756	0.0366	42.29	42.52
IV.	0.1605	0.0767	42.29	41.99

*Thorium and Piperidine.*—Piperidine precipitated thorium salts immediately, giving a white voluminous mass which is very characteristic. It settled rapidly and was filtered almost immediately, washed, dried and ignited to white thorium dioxide, heating with the blast-lamp until a constant weight was obtained. The results were:

	Salt taken. Gram.	ThO <sub>2</sub> found. Gram.	Required. Per cent.	Found. Per cent.
I.	0.1083	0.0525	42.29	42.57
II.	0.1512	0.0728	42.29	42.29
III.	0.0756	0.0360	42.29	41.78
IV.	0.1605	0.0769	42.29	42.10
V.	0.4701	0.2270	42.29	42.33

*Thorium and Quinoline.*—Quinoline gave a glistening white semi-transparent precipitate. The reaction seemed complete after standing twenty-four hours. It filtered with much greater readiness than the substituted anilines. The determinations were as follows:

	Salt taken. Gram.	ThO <sub>2</sub> found. Gram.	Required. Per cent.	Found. Per cent.
I.	0.1083	0.0522	42.29	42.35
II.	0.1083	0.0510	42.29	41.37
III.	0.1605	0.0770	42.29	42.16

Benzylamine was not tried on account of lack of material.

Phenylhydrazine with thorium salts gave a canary-yellow flocculent precipitate readily soluble in excess.

Diphenylamine was not tried.

In all of the analyses of the thorium salts the volume of liquid never was greater than 100 cc. and usually not above 50 cc.

It will be observed that while thorium responds quantitatively

to the same bases to which zirconium responded, and while the results are quantitative in character, the time factor in many cases is so extended that the application of these precipitants offers nothing of advantage to the analyst either in the direction of completeness of precipitation or rapidity of reaction.

Zirconium and thorium represent a rather wide range in atomic weights (90-232), and as the second has probably acquired somewhat more of the acid nature, this may account for the sluggishness of its behavior with the bases which were applied to it. This led to the introduction of cerium in the study, being a member of the same Group IV of the Periodic System with zirconium and thorium, and standing midway as it were in atomic weight (140) between them. The behavior of the chosen bases upon its salts was awaited with deep interest. Here, too, it may be added, that the precipitates in thorium solutions are from their very nature and behavior definite double salts. None of them showed the usual appearance of thorium hydroxide.

### III. CERIUM.

The salt used was a ceric ammonium nitrate, orange-red in color.

*Cerium and Aniline.*—A definite amount of the cerium double salt was weighed and dissolved in about 50 cc. of water, and aniline added with constant stirring. A white heavy flocculent precipitate formed almost immediately, and the liquid went through various changes in color, finally becoming nearly colorless. After standing an hour or two, the solution was filtered and the precipitate was washed, dried, ignited, and weighed as cerium dioxide, yellow to reddish yellow in color. Throughout the work, the cerium dioxide was ignited to constant weight with the blast-lamp before weighing, as directed under zirconium. The following results were obtained:

	Salt taken.	CeO <sub>2</sub> found.	Required.	Found.
	Gram.	Gram.	Per cent.	Per cent.
I.	0.4134	0.1281	25.13	25.22
II.	0.3554	0.1089	25.13	24.93
III.	0.3973	0.1254	25.13	25.69
IV.	0.3637	0.1113	25.13	24.91
V.	0.1996	0.0622	25.13	25.35

*Cerium and o-Toluidine.*—A white flocculent precipitate was formed by adding *o*-toluidine to a solution of the cerium salt and thoroughly agitating. The mass settled nicely, and after standing several hours was filtered, washed and ignited.

	Salt taken. Gram.	CeO <sub>2</sub> found. Gram.	Required. Per cent.	Found. Per cent.
I.	0.0785	0.0245	25.13	25.35
II.	0.1682	0.0513	25.13	24.82
III.	0.1210	0.0377	25.13	25.17

*Cerium and Xylidine.*—Xylidine gave a heavy white precipitate that remained suspended for some time. After stirring very thoroughly the beaker was set aside for several hours, then filtered, using a suction-pump, washed, ignited and weighed. As the results failed to show a concordance the reaction seems not to have taken place quantitatively.

	Salt taken. Gram.	CeO <sub>2</sub> found. Gram.	Required. Per cent.	Found. Per cent.
I.	0.2106	0.0483	25.13	18.66
II.	0.1890	0.0460	25.13	19.79
III.	0.2368	0.0447	25.13	15.36

*Cerium and Dimethyl Aniline.*—Cerium was precipitated with dimethyl aniline with constant stirring. A yellowish white precipitate formed and the liquid changed color rapidly, green, purple and finally nearly colorless. After standing a couple of hours it was filtered and weighed as cerium dioxide. The reaction was not quantitative, as the percentages obtained showed great variation, and the results were unsatisfactory.

	Salt taken. Gram.	CeO <sub>2</sub> found. Gram.	Required. Per cent.	Found. Per cent.
I.	0.1418	0.0312	25.13	17.91
II.	0.0899	0.0214	25.13	19.34
III.	0.0899	0.0151	25.13	13.66

*Cerium and Diethyl Aniline.*—Diethyl aniline gave a white flocculent precipitate which settled with comparative readiness, the solution becoming brown, green, purple, and finally colorless. After standing for two hours it was filtered using a suction-pump.



Cerium dioxide ultimately obtained was ignited to constant weight with the blast-lamp.

	Salt taken.	CeO <sub>2</sub> found.	Required.	Found.
	Gram.	Gram.	Per cent.	Per cent.
I.	0.1785	0.0566	25.13	25.80
II.	0.0899	0.0273	25.13	24.68
III.	0.0899	0.0290	25.13	26.24
IV.	0.0899	0.0285	25.13	25.78

*Cerium and Benzylamine.*—When benzylamine was added to a cerium salt with constant stirring, a heavy flocculent precipitate formed, which rapidly changed in color, becoming brown and finally nearly black. The precipitate settled rapidly and was filtered after standing several hours without the use of a suction-pump.

	Salt taken.	CeO <sub>2</sub> found.	Required.	Found.
	Gram.	Gram.	Per cent.	Per cent.
I.	0.1142	0.0345	25.13	24.59
II.	0.1192	0.0375	25.13	25.59

*Cerium and Pyridine.*—Pyridine gave a beautiful white glistening precipitate that settled rapidly and filtered quickly and easily. It was very gelatinous. The results were quantitative.

	Salt taken.	CeO <sub>2</sub> found.	Required.	Found.
	Gram.	Gram.	Per cent.	Per cent.
I.	0.1932	0.0609	25.13	25.65
II.	0.1192	0.0372	25.13	25.39
III.	0.2488	0.0775	25.13	25.35

*Cerium and Piperidine.*—Piperidine also gave a white precipitate, and its physical properties closely resembled those observed in the precipitate obtained with pyridine. The quantitative results were:

	Salt taken.	CeO <sub>2</sub> found.	Required.	Found.
	Gram.	Gram.	Per cent.	Per cent.
I.	0.2005	0.0631	25.13	25.62
II.	0.2248	0.0695	25.13	25.16
III.	0.1156	0.0360	25.13	25.35
IV.	0.2011	0.0635	25.13	25.70

*Cerium and Quinoline.*—Quinoline seemed not to give a quantitative reaction. I thought at first that the variation in results might be due to the fact that the quinoline used contained brown substances and that the excess of the precipitant clung to the sides of the beaker and was very difficult to remove, even when a glass rod with a rubber cap was used. It was thought that perhaps some of the precipitate might be lost in this way, so an alcoholic wash was used, and also chloroform, which completely removed the excess of quinoline from the beaker, but the final results were unsatisfactory.

	Salt taken. Gram.	CeO <sub>2</sub> found. Gram.	Required. Per cent.	Found. Per cent.
I.	0.5027	0.1058	25.13	17.13
II.	0.2898	0.0591	25.13	16.60
III.	0.1720	0.0354	25.13	16.74
IV.	0.1364	0.0337	25.13	20.09
V.	0.2306	0.0326	25.13	11.49

In Experiment IV alcohol was used, and chloroform in Experiment V.

Both phenylhydrazine and diphenylamine failed to precipitate cerium salts.

Strangely enough, several of the bases failed to yield quantitative results. With xylydine this may be due to the presence of the additional methyl group; perhaps, too, in dimethyl aniline, the accumulation of positive substituents is the cause of the failure in reaction; if so, why should not the same occur in the use of diethyl aniline where quantitative precipitation does take place? The slight basicity of diphenylamine explains its failure, but the lack of action in quinoline is not so readily comprehended.

A glance at the arrangement of the elements in the Periodic System shows that directly opposite—preceding cerium—as a member of Group III, appears lanthanum, while following cerium in Group V, are neodymium and praseodymium. Would their conduct with the selected bases bring to light any unobserved facts? Lanthanum following in its oxide the type  $R_2O_3$ —a type readily precipitated by ammonia—might perhaps shed some light on the behavior of cerium, and account for the variations observed

between it and its associates of Group IV. Therefore, it was next considered in the proposed study.

#### IV. LANTHANUM.

Two salts of lanthanum were used, the chloride and the double nitrate with ammonium.

Aniline *o*-toluidine and xyloidine all failed to precipitate lanthanum salts. Dimethyl aniline also gave no reaction, and diethyl aniline after long standing gave a slight film at the point of contact, though no precipitate was discernible.

*Lanthanum and Benzylamine.*—Benzylamine gave with lanthanum salts, as with the metals previously tested, a heavy white flocculent precipitate. When the resulting oxide was ignited to constant weight, it gave the following percentages:

	Salt taken. Gram.	La <sub>2</sub> O <sub>3</sub> found. Gram.	Required. Per cent.	Found. Per cent.
I.	0.1685	0.0741	37.94	37.50
II.	0.2051	0.0628	24.96	26.11

*Lanthanum and Pyridine.*—At first no precipitate formed, but after standing several days a very fine white precipitate separated. It was granular and shining in appearance, and like that obtained with praseodymium, clung very closely to the beaker, and was only removed with the greatest difficulty, and showed a tendency to run through the filter-paper.

The results were not quantitative.

*Lanthanum and Piperidine.*—Piperidine gave a white glistening gelatinous precipitate, similar in properties to that obtained by the same reagent with the metals already mentioned.

	Salt taken. Gram.	La <sub>2</sub> O <sub>3</sub> found. Gram.	Required. Per cent.	Found. Per cent.
I.	0.1580	0.0705	37.94	38.04
II.	0.1713	0.0750	37.94	37.33
III.	0.2106	0.0937	37.94	37.94
IV.	0.3826	0.1141	24.96	25.43

Diphenylamine was not tried, and quinoline failed to show any reaction.

Phenylhydrazine gave a flocculent reddish brown precipitate which grew less on standing.

Only those bases having a decidedly basic nature—benzylamine and piperidine—seem capable of throwing out lanthanum completely. Eight of them apparently fail of this end, and in this behavior is found a hint as to what cerium might be expected to do. It accordingly became still more interesting to ascertain the deportment of praseodymium and neodymium in the indicated directions.

#### V. PRASEODYMIUM.

Two salts were used,  $\text{Pr}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ , and the double nitrate  $\text{Pr}(\text{NO}_3)_3 \cdot 2\text{NH}_4\text{NO}_3 \cdot 4\text{H}_2\text{O}$ , both green in color.

Aniline and praseodymium appeared not to react, although the behavior was rather confusing. Tests were made, but no precipitate formed even after long standing, but later, when the tests were repeated, it was found that when the test-tube stood in a warm place, a slight precipitate did form, which on long standing again disappeared.

Neither *o*-toluidine nor xylidine gave evidence of any reaction with praseo-salts even after long standing. Dimethyl aniline gave no precipitate and diethyl aniline behaved in a similar manner, though after standing for a long time, a very slight sum was noticed at the point of contact.

*Praseodymium and Benzylamine.*—Benzylamine gave a white flocculent precipitate, very voluminous which, like many of the preceding precipitates, filtered rapidly, after standing several hours. The resulting brown-black oxide, after ignition with the blast-lamp, gave the following:

	Salt taken.	$\text{Pr}_2\text{O}_3$ found.	Required.	Found.
	Gram.	Gram.	Per cent.	Per cent.
I.	0.1348	0.0520	32.57	32.20

*Praseodymium and Pyridine.*—When pyridine was first added, no reaction seemed to take place, but on standing, a fine white granular precipitate separated on the bottom of the beaker. It was filtered and estimated as usual. The precipitate clung closely to the sides of the beaker, and it was almost impossible to thor-

oughly remove it. One analysis was made, and the result was unsatisfactory.

*Praseodymium and Piperidine.*—Piperidine gave a white, glistening, gelatinous precipitate, with a slight greenish tinge. Its properties were very similar to the neodymium-piperidine precipitate. Like the latter, it was found best to dry the product simply in the air, because when heated on a metal drying cone over a Bunsen flame, the mass melted and ran through the filter, and partly disappeared. It was a quantitative reaction.

	Salt taken. Gram.	Pr <sub>2</sub> O <sub>3</sub> found. Gram.	Required. Per cent.	Found. Per cent.
I.	0.2014	0.0788	32.57	32.67
II.	0.0970	0.0380	32.57	32.68
III.	0.0979	0.0378	32.57	32.22

Quinoline gave no precipitate, and the action of diphenylamine was not tried. Phenylhydrazine gave a flocculent reddish brown precipitate, which on standing partly disappeared.

Comparison with the behavior of lanthanum reveals the fact that these two elements behave almost analogously with the bases brought in contact with them and vary in about the same degree from cerium.

#### VI. NEODYMIUM.

*Neodymium and Aniline.*—When aniline was added to a neodymium solution at first no reaction seemed to take place, but after the beaker had stood some time, a slight gelatinous precipitate separated, white in color. After several hours the liquid was filtered, and the resulting blue-brown sesquioxide weighed. The reaction was not quantitative.

	Salt taken. Gram.	Nd <sub>2</sub> O <sub>3</sub> found. Gram.	Required. Per cent.	Found. Per cent.
I.	0.09855	0.0139	32.57	12.06
II.	0.09855	0.0109	32.57	9.44
III.	0.09855	0.0236	32.57	20.48

*o*-Toluidine gave no precipitate. Xylidine after long standing gave a very slight yellowish white flocculent mass. Dimethyl ani-

line at first failed to react, but after some time had elapsed a faint film was noticed.

Diethyl aniline showed a slight precipitate, yellowish white in color, but the result obtained was far from quantitative.

*Neodymium and Benzylamine.*—Benzylamine gave a voluminous white precipitate, which separated in small beautiful floc-cules. The result was quantitative.

	Salt taken.	Nd <sub>2</sub> O <sub>3</sub> found.	Required.	Found.
	Gram.	Gram.	Per cent.	Per cent.
I.	0.1608	0.0611	32.57	32.50

*Neodymium and Pyridine.*—Pyridine after standing a short time gave a slight yellowish white precipitate. The reaction was in-complete.

*Neodymium and Piperidine.*—The neodymium salt was im-mediately precipitated, giving a glistening white product, with a faint violet tinge. It was very gelatinous, but readily filtered, and gave results closely corresponding to the theoretical. It was dried simply in the air, for when I attempted to dry it upon a stove-plate, using a metal cone, the precipitate melted and ran through the filter-paper.

	Salt taken.	Nd <sub>2</sub> O <sub>3</sub> found.	Required.	Found.
	Gram.	Gram.	Per cent.	Per cent.
I	0.2912	0.1135	32.57	33.44
II.	0.0985	0.0378	32.57	32.78
III	0.1471	0.0436	25.36	25.35
IV	0.1869	0.0557	25.36	25.47

Quinoline failed to react. No attempt was made to precipitate neodymium salts with diphenylamine. Phenylhydrazine gave a fine orange-red flocculent mass, which on standing appreciably decreased in bulk, finally disappearing almost entirely.

The behavior of praseodymium is here repeated. In almost every particular the representatives of Group V conduct them-selves similarly, and manifest a decided relationship, from the present point of study, to lanthanum, whereas they differ markedly from cerium. May not the obvious conduct of cerium with the different precipitants enumerated in the preceding paragraphs, be

safely regarded as decided evidence of the true position of cerium in the periodic classification. Is not its deportment with these bases more in harmony with that of zirconium and thorium than with that of lanthanum, neodymium, and praseodymium? Its juxtaposition to the latter unquestionably explains why it is not precipitated by xylydine, dimethyl aniline and quinoline, with all of which its natural associates gave quantitative precipitations.

#### SEPARATIONS.

Having made the observation that many of the precipitations described were quantitative, and that other salts with the same reagents failed to react at all, the thought arose that probably separations could be made, and accordingly investigations along these lines were begun. The results of these attempts are given in the following pages. The field seems to be a large one, by no means exhausted, and the possibilities appear great.

*I. Separation of Thorium and Neodymium by Quinoline.*—A known amount of the thorium solution diluted to approximately 50 cc. was placed in a beaker, and a weighed quantity of the neodymium salt added. Quinoline was then added with constant stirring and the beaker set aside for twenty-four hours. It was then carefully filtered and washed thoroughly, the beaker containing the neodymium filtrate removed, and a fresh vessel substituted. The precipitate while still moist was dissolved in dilute hydrochloric acid or preferably dilute nitric acid, and the filter-paper washed thoroughly with water to remove the last traces of the acid solution. It was found advisable to use as little acid as possible to prevent the final dilution from being unnecessarily great.

The acid solution was next neutralized as nearly as possible with ammonia water. A little nicety in manipulation was required, because if too great an amount of ammonia were added, the metals would be precipitated, while, on the other hand, too large an excess of acid would retard the reprecipitation by quinoline, making the final results too low. Leaving the solution very slightly acid, quinoline was again added, and the liquid agitated. The reaction commenced almost immediately, and in every case it

was noticed that the reprecipitation gave a mass much more flocculent than that obtained by simply precipitating once.

After twenty-four hours, the solution was filtered, adding this filtrate to the first one, and the precipitate washed, dried, ignited with the blast lamp to constant weight, and determined as thorium dioxide. The reprecipitation was found necessary, because when the thorium was only precipitated once, the resulting oxide showed a very faint color of neodymium, whereas the thorium dioxide obtained by dissolving and reprecipitating was in every case pure and white without the slightest trace of the blue-brown oxide of neodymium.

	Salt taken. Gram.	ThO <sub>2</sub> found. Gram.	Required. Per cent.	Found. Per cent.
I.	0.15466	0.0751	42.29	42.67
II.	0.15466	0.0746	42.29	42.38
III.	0.1206	0.0581	42.29	42.33
IV.	0.15157	0.0734	42.29	42.55
V.	0.15157	0.0724	42.29	41.96
VI.	0.15157	0.0728	42.29	42.20
VII.	0.15157	0.0740	42.29	42.88

## II. Separation of Zirconium and Neodymium by Quinoline.—

The separation was carried out exactly as directed under thorium, but in each case the precipitate stood twelve hours instead of twenty-four hours. The same precautions were observed. The results are appended.

	Salt taken. Gram.	ZrO <sub>2</sub> found. Gram.	Required. Per cent.	Found. Per cent.
I.	0.14406	0.0595	30.30	30.47
II.	0.14406	0.0590	30.30	30.20
III.	0.14406	0.0582	30.30	29.78
IV.	0.10948	0.0448	30.30	30.14
V.	0.15084	0.0462	22.90	22.59
VI.	0.15084	0.0471	22.90	23.00

Here also, the resulting zirconium dioxide was white, not the slightest trace of the color of the neodymium oxide being perceptible, but the neodymium percentages were too high when determined by ammonia in the filtrate. In each of the separations described the resulting filtrates were precipitated with pure am-



monia, but in every case the resulting percentages were found to be somewhat too high when compared with the theoretical.

	Salt taken. Gram.	Nd <sub>2</sub> O <sub>3</sub> found. Gram.	Required. Per cent.	Found. Per cent.
I.	0.2092	0.0624	25.36	25.51
II.	0.1433	0.0435	25.36	25.96
III.	0.1291	0.0837	25.36	26.19
IV.	0.1442			

Zirconium and ammonia, the resulting mean, used as the unit of comparison:

	Salt taken. Gram.	ZrO <sub>2</sub> found. Gram.	Found. Per cent.	Mean. Per cent.
I.	0.14406	0.0587	30.05	
II.	0.14406	0.0597	30.54	30.30
I.	0.15084	0.0468	22.87	
II.	0.15084	0.0469	22.93	22.90

*III. Separation of Thorium and Lanthanum by Aniline.*—The procedure was exactly as directed under quinoline, and both times the precipitate stood twenty-four hours before filtering. It was advantageous to allow the excess of the precipitant to filter through, and then wash the precipitate with water before dissolving in dilute nitric acid, because otherwise the organic material in solution rendered it darker in color, and it was more difficult to decide when the point of neutralization was being approached. As the oxides of thorium and lanthanum are both white, it was, of course, not possible to tell whether the final thorium dioxide contained a slight amount of lanthanum by the color, as was done with the blue-brown neodymium oxide. Therefore, endeavoring to make the results as accurate as possible, the weighed thorium dioxide, was in each case treated in the crucible with concentrated hydrochloric acid or nitric acid, and allowed to stand several hours.

As the lanthanum sesquioxide is soluble in acids, it should dissolve leaving the thorium dioxide. The acid solution was poured quickly into a small beaker and the precipitate of thorium dioxide washed into the beaker with water. If care be taken, no milkiness

will be noticed. The liquid was then filtered, the precipitate ignited to constant weight, and finally weighed as thorium dioxide. The filtrate which would contain the trace of lanthanum if present, was added to the first filtrate known to contain the lanthanum from the separation. The final results were as follows:

	Salt taken. Gram.	ThO <sub>2</sub> found. Gram.	Required. Per cent.	Found. Per cent.
I.	0.3210	0.1550	42.29	42.43
II.	0.3210	0.1552	42.29	42.49
III.	0.3210	0.1550	42.29	42.43
IV.	0.3210	0.1552	42.29	42.49
V.	0.3210	0.1554	42.29	42.54

*IV. Separation of Zirconium and Lanthanum by Aniline.—*

The reaction was carried out exactly as directed under the separation of thorium and lanthanum by aniline, except that in each case the time factor was twelve hours instead of twenty-four. The resulting zirconium dioxide was treated with concentrated hydrochloric or nitric acid to dissolve out any trace of lanthanum.

	Salt taken. Gram.	ZrO <sub>2</sub> found. Gram.	Required. Per cent.	Found. Per cent.
I.	0.13458	0.0576	31.96	31.57
II.	0.2539	0.1034	30.13	30.04
III.	0.2539	0.1036	30.13	30.09
IV.	0.2539	0.1043	30.13	30.29

*Zirconium and Ammonium Hydroxide.*

	Salt taken. Gram.	ZrO <sub>2</sub> found. Gram.	Found. Per cent.	Mean. Per cent.
I.	0.2539	0.1040	30.21	
II.	0.2539	0.1034	30.04	30.13
I.	0.1345	0.0586	32.10	
II.	0.2045	0.0883	31.82	31.96

*V. Separation of Thorium and Lanthanum by Quinoline.—*A known number of cubic centimeters of the thorium solution, and a weighed quantity of the lanthanum salt, were placed in a small beaker, diluted to about 50-75 cc. and quinoline added, stirring the liquid very thoroughly. The subsequent operations were carried out in a manner quite similar to that described in the preceding

experiments. The precipitate was allowed to stand twenty-four hours each time. The final thorium dioxide obtained was treated with concentrated acid, to remove any lanthanum that might have been carried down by the thorium.

	Salt taken. Gram.	ThO <sub>2</sub> found. Gram.	Required. Per cent.	Found. Per cent.
I.	0.3318	0.1577	42.29	41.77
II.	0.3318	0.1592	42.29	42.16
III.	0.3318	0.1581	42.29	41.86
IV.	0.3318	0.1585	42.29	41.98
V.	0.3318	0.1582	42.29	41.89

*VI. Separation of Cerium and Praseodymium by o-Toluidine.*—

After ascertaining the fact that *o*-toluidine precipitated cerium salts quantitatively, and with the salts of neodymium gave no reaction, I endeavored to separate the two, using this means. It was found by experiment that if the precipitate of cerium were dissolved in acid, it refused to be reprecipitated when, after neutralizing, an excess of the precipitant was again added. Consequently, *o*-toluidine was added only once, and no attempt was made to dissolve and reprecipitate.

The experiment was made, using from 50-75 cc. of solution, and allowing the precipitate to stand over night before filtering. The resulting cerium dioxide seemed rather darker in color than usual, which may have been due to a trace of praseodymium oxide, notwithstanding the fact that the weight of the cerium dioxide found agreed with the theoretical within the limit of experimental error.

	Salt taken. Gram.	CeO <sub>2</sub> found. Gram.	Required. Per cent.	Found. Per cent.
I.	0.1750	0.0543	25.13	25.25

*VII. Separation of Thorium and Praseodymium by Aniline.*—

The confusing behavior of praseodymium with aniline has already been mentioned. I am inclined to think that possibly conditions such as temperature, concentration, etc., influence it, because when a test-tube containing the two stood in a warm place, a slight precipitate formed, which was quite perceptible, but after standing for some time in the cold, it entirely disappeared. At another time aniline and praseodymium stood in contact for months, without

any precipitate separating out. Another thought is that perhaps even if the conditions were such as to allow a precipitate to form, possibly the small amount of acid present in the solution after dissolving the thorium precipitate in acid and almost neutralizing, would be sufficient to prevent any reaction between the two.

Accordingly, an attempt was made to separate thorium from praseodymium using aniline as the precipitant. The method was quite similar to that pursued in the foregoing separations, the precipitate being allowed to stand each time for twenty-four hours. The mass first obtained was dissolved in dilute nitric acid, carefully neutralized and reprecipitated. The thorium dioxide ultimately obtained was treated in the cold with concentrated nitric acid, allowing it to remain undisturbed for two hours, hoping in this way to remove the slight trace of color noticed. After filtering, washing and igniting, a *very* faint brownish tinge was always noticed. The weights corresponded quite well with the theoretical but at no time was the resulting thorium dioxide absolutely white. Even after treatment with nitric acid, the thorium dioxide showed a slight tinge of color, upon close examination.

	Salt taken.	ThO <sub>2</sub> found.	Required.	Found.
	Gram.	Gram.	Per cent.	Per cent.
I.	0.3318	0.1600	42.29 .	42.37
II.	0.3318	0.1592	42.29	42.16
III.	0.3318	0.1600	42.29	42.37
IV.	0.3318	0.1602	42.29	42.43

An attempt was made to separate zirconium and praseodymium using *o*-toluidine. Only one analysis was attempted, and the result was rather low, but near enough to indicate the probability of such a separation being made under proper conditions. The zirconium dioxide obtained was perfectly white in color.

*VIII. Separation of Zirconium and Lanthanum by Xylidine.*—As previously stated, xylidine precipitates zirconium quantitatively, so an attempt was made to separate zirconium from lanthanum using it as the medium. Xylidine was added to the solution containing the two salts, with constant agitation. The precipitate formed almost immediately, but as a matter of precaution it was allowed to stand over night. In the morning it was filtered, al-

lowing the excess of xylidine to run through the filter, washing thoroughly with water, and then with 95 per cent. alcohol, till the brown color of the xylidine had disappeared and the precipitate and filter were clean and white. It was then again washed with water, dissolved in dilute nitric acid and almost neutralized with ammonium hydroxide, leaving the solution very slightly acid. After reprecipitating with xylidine it was allowed to stand twelve hours, and again filtered, finally estimating as zirconium dioxide. The resulting oxide was treated for two hours in the cold with concentrated nitric acid, then filtered and determined as usual.

	Salt taken. Gram.	ZrO <sub>2</sub> found. Gram.	Required. Per cent.	Found. Per cent.
I.	0.2158	0.0864	29.69	29.52

*Zirconium and Ammonia:*

	Salt taken. Gram.	ZrO <sub>2</sub> found. Gram.	Found. Per cent.	Mean. Per cent.
I.	0.2158	0.0863	29.50	
II.	0.2158	0.0874	29.87	29.69

If nitric acid were added to dissolve the precipitate in the separation of lanthanum and zirconium by xylidine, without previously washing with alcohol, the excess of xylidine would combine with the nitric acid, giving an organic precipitate so dense that it would prevent one from seeing when the point of neutralization was approaching in the subsequent treatment with ammonium hydroxide, hence the advisability of using an alcoholic wash.

*IX. Separation of Zirconium and Praseodymium by Xylidine.*—

An attempt was made to separate these two in a manner perfectly analogous to that just described. The resulting zirconium dioxide was light yellow in color, though the weight corresponded with that required.

	Salt taken. Gram.	ZrO <sub>2</sub> found. Gram.	Required. Per cent.	Found. Per cent.
I.	0.2158	0.0867	29.69	29.63

SUMMARY.

Six metals were acted upon by characteristic aromatic bases, when it was found that zirconium is precipitated quantitatively

by nearly all of them. Thorium is precipitated by aniline, *o*-toluidine, xyloidine, diethyl aniline, dimethyl aniline, pyridine, piperidine and quinoline. Aniline *o*-toluidine, diethyl aniline, benzylamine, pyridine and piperidine are the only precipitants of cerium, while with lanthanum, neodymium and praseodymium, the precipitants are benzylamine and piperidine.

Quinoline will separate thorium from neodymium and zirconium from the latter, while aniline separates thorium and also zirconium from lanthanum. The latter and thorium are also separated by quinoline. With *o*-toluidine cerium may be separated from praseodymium, and the latter and thorium may be separated by aniline. Finally, xyloidine will separate zirconium from lanthanum, as well as from praseodymium.

UNIVERSITY OF PENNSYLVANIA.

---

## A NEW METHOD FOR THE APPROXIMATE DETERMINATION OF URIC ACID IN URINE.

BY JULIUS RUDISCH AND LEOPOLD BOROSCHKE.

Received March 13, 1902.

SEVERAL of the most important methods for the quantitative determination of uric acid in urine, depend on the practically complete precipitation of the uric acid, as a magnesia silver urate, by the addition of an ammoniacal silver solution and a magnesia solution to the urine.

This method of precipitation is open to several objections:

First, the ammoniacal magnesia solution causes a voluminous precipitate of triple phosphate to separate from the urine. This precipitate, if not previously removed, contaminates the silver urate precipitate, rendering filtration and washing difficult owing to its large bulk. In Ludwig's method<sup>1</sup> the phosphates are thrown down together with the uric acid. Salkowski<sup>2</sup> recommends the removal of the phosphates by means of an ammoniacal magnesia solution and filtering the urine, previous to the addition of the ammoniacal silver solution. Folin and Shaffer found<sup>3</sup> that if this

<sup>1</sup> *Ztschr. anal. Chem.*, 21, 148 (1882).

<sup>2</sup> *Ztschr. physiol. Chem.*, 14, 50 (1890).

<sup>3</sup> *Ibid.*, 32, 553 (1901).

method be followed, a loss of about 0.002 gram of uric acid for 100 cc. of urine results.

Second, the ammoniacal silver solution not only precipitates the uric acid but also the xanthine bases contained in the urine.

Third, the silver precipitate obtained by this method from urine, is not entirely insoluble in dilute solutions of ammonia.

Fourth, the precipitate is generally dark colored, or gradually blackens owing to a reduction of the ammonia silver solution. Salkowski<sup>1</sup> also noticed this. Haycraft<sup>2</sup> and Herman<sup>3</sup> found that the addition of sodium bicarbonate hinders but does not entirely prevent this reduction.

In an attempt to do away with the use of ammonia to which at least three of the above-mentioned difficulties could be traced, a sulphite-silver solution was tried.

The solubility of silver chloride in an aqueous solution of sodium sulphite is not generally known, as no mention of it can be found in Comey's "Dictionary of Chemical Solubilities."

It was found by us that at ordinary room temperature, 100 cc. of a saturated aqueous solution of sodium sulphite dissolves about 1 gram of silver chloride. In the experimental work a twentieth normal solution, containing 7.175 grams of silver chloride in 1 liter was employed.

By adding the sulphite-silver solution, to a solution of uric acid, strongly alkaline with sodium carbonate, it was found that all the uric acid was thrown down as an almost white, flocculent precipitate which settles after several minutes and which can be readily filtered out and washed. This precipitate dissolves to a considerable extent in cold water, but is practically insoluble in dilute solutions of sodium carbonate.

From the analyses of the precipitate, the ratio of silver to nitrogen was found to agree with that calculated for 1 atom of silver to 1 molecule of uric acid. From the fact that the uric acid is completely precipitated in the absence of magnesia salts, and also that uric acid cannot form neutral salts with alkalis in the presence of carbon dioxide or soluble carbonates as claimed by Allen and

<sup>1</sup> *Ztschr. physiol. Chem.*, 14, 40 (1890).

<sup>2</sup> *Ztschr. anal. Chem.*, 25, 169 (1886).

<sup>3</sup> *Ztschr. physiol. Chem.*, 12, 497.

Beusch<sup>1</sup>, further, from the conditions under which the precipitation was made, it is probable that the precipitate has the following composition:  $\text{AgC}_2\text{H}_3\text{N}_4\text{O}_3$ .

When the sulphite-silver solution is added to urine, made strongly alkaline with sodium carbonate, a yellowish white flocculent precipitate forms, which settles after a few minutes and can be readily filtered out and washed. The precipitate does not darken during washing, or on exposure to the air. By this method the voluminous precipitate of the triple phosphates is avoided, as the addition of a considerable excess of a saturated sodium carbonate solution, to the urine, throws down only a slight precipitate. This need not be removed previous to the addition of the sulphite-silver solution. By adding from 10 to 15 grams of Rochelle salt to 100 cc. of urine it will remain clear even after the addition of an excess of a sodium carbonate solution.

A series of parallel determinations upon a number of urines were made, using both the silver-ammonia and the sulphite-silver methods of precipitation. The silver or nitrogen or both of these constituents of the precipitates were determined. By calculating all the results to uric acid, it was found that those obtained by the silver-ammonia method were from 0.001 to 0.006 gram (uric acid) higher for 100 cc. of urine, than the results obtained by the sulphite silver method.

On examining the precipitates obtained by both methods, according to the Salkowski<sup>2</sup> method for the determination of xanthenes, it was found, that the difference in the results obtained by the two methods could be partly, if not entirely accounted for, by the fact that the sulphite-silver solution does not precipitate the xanthine bases as completely as the ammonia-silver solution. Which of the 10 xanthine bases that have been discovered in urine are, and which are not, precipitated by the sulphite-silver solution has not as yet been determined.

#### EXPERIMENTAL PART.

##### *A. Uric Acid.*

1. 0.150 gram uric acid was dissolved in a hot solution of sodium

<sup>1</sup> *Ann. Chem. Pharm.*, 63, 181 (1848).

<sup>2</sup> *Pflüger's Archiv.*, 69, 280 (1898).



carbonate and diluted to 300 cc. with water. An excess of a magnesium nitrate solution and 30 cc. of twentieth-normal sulphite-silver solution were added. After standing one-half hour, the precipitate was filtered off and washed free of the excess of silver and of chlorine with water. The precipitate and filter were digested in a Kjeldahl flask with concentrated sulphuric acid and potassium sulphate, and heated until almost colorless. On cooling, the mixture was diluted with water, the silver was separated as silver sulphide, by means of a sodium sulphide solution, and after being filtered out and washed was determined by the Volhard method. The filtrate was made alkaline with sodium hydroxide and the ammonia was distilled into a standard sulphuric acid solution.

The silver required 7 cc. of tenth-normal ammonium thiocyanate.

$$7 \times 0.0168 = 0.1176 \text{ gram uric acid.}$$

The ammonia neutralized 28 cc. of tenth-normal sulphuric acid.

$$28 \times 0.0014 \times 3 = 0.1176 \text{ gram uric acid.}$$

The ratio of the silver to nitrogen corresponds to 1 atom of silver to the molecule of uric acid. It was afterwards found that the loss of uric acid was due to the solubility of the precipitate in water.

2. 0.250 gram of uric acid was dissolved in a dilute potassium hydroxide solution (free from chlorine) and made up to 500 cc. with water.

100 cc. of this solution was titrated according to Hopkins' method. Required 13.1 cc. of twentieth-normal potassium permanganate.

$$13.1 \times 3.75 = 0.0491 \text{ gram uric acid.}$$

To 250 cc. of this solution, an excess of magnesium nitrate solution was added, 25 cc. of a saturated aqueous sodium carbonate solution, and 25 cc. of twentieth-normal sulphite-silver solution. The precipitate was filtered off and washed with a dilute solution of sodium carbonate. To the first wash solution a little sodium sulphite was also added. The precipitate and filter were placed in a beaker and boiled with concentrated nitric acid (free of chlorine). Then it was diluted with water and boiled to expel the

oxides of nitrogen. When cold the solution was titrated with a thiocyanate solution, using ferric alum as an indicator.

Required 36.6 cc. fiftieth-normal ammonium thiocyanate.

$$\frac{36.6 \times 2 \times 0.00168}{2.5} = 0.0492 \text{ gram uric acid for 100 cc. of the solution.}$$

3. A solution of 0.250 gram of uric acid in 500 cc. was made as in (2).

I. 100 cc. by Hopkins' method required 13.3 cc. twentieth-normal potassium permanganate.

II. 100 cc. by Hopkins' method required 13.3 cc. twentieth-normal potassium permanganate.

$13.3 \times 3.75 = 0.0499$  gram uric acid in 100 cc of the solution.

To 100 cc. of the solution, 15 cc. of a saturated solution of sodium carbonate, and 10 cc. of twentieth-normal sulphite-silver solution were added. The precipitate was treated as in (2). Required 14.7 cc. of fiftieth-normal ammonium thiocyanate = 0.0494 gram uric acid.

Another 100 cc. was treated in exactly the same way. Required 14.8 cc. of fiftieth-normal ammonium thiocyanate = 0.0497 gram uric acid.

Therefore the uric acid was completely precipitated by the sulphite-silver solution in the absence of magnesium salts.

### B. *Experiments with Urine.*

The following methods of precipitation were employed:

1. *The Sulphite-Silver Method.*—A measured amount of urine was taken. After neutralizing with a saturated aqueous solution of sodium carbonate, 15 cc. excess for each 100 cc. of urine was added, and then 10 cc. of twentieth-normal sulphite-silver solution was added. In many of the determinations an excess of magnesium nitrate solution was also introduced, but this was found to be unnecessary. After standing one hour, the precipitate was filtered off and washed free of the excess of silver and of chlorine with a dilute solution of sodium carbonate.

2. *The Ammonia-Silver Method.*—A measured amount of urine was taken. For each 100 cc. was added 10 cc. of the Ludwig mag-

nesia mixture. The urine was then diluted to a known bulk and filtered through a dry filter. An aliquot portion of the filtrate was taken and for each 100 cc. urine represented by the filtrate 5 cc. of a tenth-normal ammoniacal silver solution was added. After standing one hour, the precipitate was filtered off and washed free of the excess of silver and of chlorine with a very dilute ammonia solution. If the nitrogen of the precipitate was to be determined, it was washed with water to remove the ammonia.

To determine the silver and nitrogen contained in these precipitates the filter and precipitate were boiled with water containing a little magnesium oxide to remove the last traces of ammonia, and then the method as described under A 1 was followed. When only the silver contained in these precipitates was to be determined, the method described under A 2 was used. The results are given in the following table:

Urine.	Method of precipitation.	Silver per 100 cc. of urine.	Silver calculated to uric acid.	Nitrogen per 100 cc. of urine.	Nitrogen calculated to uric acid.
1	<sup>1</sup> Sulphite-silver ....	0.0404	0.063	...	...
	Ammonia-silver ...	0.0414	0.0645	...	...
2	<sup>1</sup> Sulphite-silver ....	0.0329	0.0507	...	...
	Ammonia-silver ...	0.0331	0.0517	...	...
3	<sup>1</sup> Sulphite-silver ....	0.0348	0.0542	0.0154	0.0462
	Sulphite-silver ....	0.0359	0.0558	...	...
	Ammonia-silver ...	0.035	0.0546	0.0164	0.0492
4	<sup>1</sup> Sulphite-silver ....	0.0301	0.0468	...	...
	Sulphite-silver ....	0.0301	0.0468	...	...
	Ammonia-silver ...	0.0339	0.0528	0.0167	0.0501
5	<sup>1</sup> Sulphite-silver ....	0.0324	0.0504	...	...
	Sulphite-silver ....	0.0324	0.0504	...	...
	Ammonia-silver ...	0.0339	0.0528	...	...
6	<sup>2</sup> Sulphite-silver ....	0.0274	0.0426	...	...
	Ammonia-silver ...	0.0291	0.0454	...	...
7	<sup>2</sup> Sulphite-silver ....	0.0346	0.0541	...	...
	Ammonia-silver ...	0.0363	0.0561	...	...
8	<sup>2</sup> Sulphite-silver ....	0.0229	0.036	0.0115	0.0346
	Ammonia-silver ...	0.0286	0.044	0.0141	0.0423

From the invariably lower results obtained by the sulphite-silver method, it was suspected that the xanthine bases of the urine were

<sup>1</sup> Magnesium solution also added.

<sup>2</sup> Mixed urine containing sugar.

not precipitated by the sulphite-silver solution. In order to determine this fact the following experiments were tried:

1. By means of the Salkowski method<sup>1</sup> the xanthine bases from 900 cc. of urine were obtained in a dilute sulphuric acid solution. This solution was diluted with water to 100 cc.

Fifty cc. of this solution were made alkaline with ammonia and the xanthine bases precipitated as silver salts by the addition of an ammoniacal silver solution. The silver contained in the precipitate was determined by the Volhard method. Required 18.4 cc. of fiftieth-normal ammonium thiocyanate.

To 50 cc. of the same solution an excess of sodium carbonate was added and then the sulphite-silver solution. The silver, in the xanthine-silver precipitate, was titrated by the Volhard method. Required 15.7 cc. of fiftieth-normal ammonium thiocyanate.

The difference in the silver content of the xanthine precipitates obtained by the two methods was therefore:

$18.4 - 15.7 = 2.7$  cc. fiftieth-normal ammonium thiocyanate = 0.0058 gram silver for 450 cc., or 0.0013 gram silver for 100 cc. of urine.

Calculated to uric acid this difference amounts to 0.002 gram per 100 cc. of urine.

2. The silver, in the precipitate from 100 cc. of a urine obtained by the sulphite-silver method, required 16.1 cc. fiftieth-normal ammonium thiocyanate.

The xanthine-silver, obtained by applying the Salkowski method to the precipitate from 300 cc. of urine thrown down by the sulphite-silver method, required 5.7 cc. of fiftieth-normal ammonium thiocyanate.

The uric acid in 100 cc. of this urine was

$$\left(16.1 - \frac{5.7}{3}\right) \times 2 \times 0.00168 = 0.0477 \text{ gram.}$$

Similarly the silver in the precipitate from 100 cc. of urine obtained by the ammonia-silver method, required 16.8 cc. of fiftieth-normal thiocyanate; and the xanthine-silver from 300 cc. of this urine obtained by the Salkowski method required 7.8 cc. of fiftieth-normal ammonium thiocyanate.

<sup>1</sup> Neubaum Vogel's "Analyse des Harns," p. 89, 10th ed.

The uric acid in 100 cc. of the urine was

$$\left(16.8 - \frac{7.8}{3}\right) \times 2 \times 0.00168 = 0.0477 \text{ gram.}$$

3. Another urine was treated in the same way.

The silver in the precipitate obtained according to the sulphite-silver method from 100 cc. of urine, required 14.8 cc of fiftieth-normal ammonium thiocyanate.

The xanthine silver, from 300 cc. of urine by sulphite-silver method, required 7.8 cc. of fiftieth-normal ammonium thiocyanate.

The uric acid in 100 cc. of the urine is

$$\left((14.8 - \frac{7.8}{3}) \times 2 \times 0.00168 = 0.041 \text{ gram.}\right.$$

The silver from 100 cc. of the urine by the silver-ammonia method, required 15.5 cc. of fiftieth-normal ammonium thiocyanate.

The xanthine silver obtained by the Salkowski method from 300 cc. of the urine, required 9 cc. of fiftieth-normal ammonium thiocyanate.

The uric acid in 100 cc. of the urine is

$$\left(15.5 - \frac{9}{3}\right) \times 2 \times 0.00168 = 0.042 \text{ gram.}$$

The difference in the results found by the two methods, can be partly accounted for by the fact that the sulphite-silver solution does not precipitate the xanthine bases completely.

The use of a sulphite-silver solution instead of an ammoniacal silver solution for the precipitation of uric acid in urine, has the advantage that by its use the precipitation of the bulky earthy phosphates is avoided, the precipitate does not darken, as no reduction of the silver solution takes place and finally the precipitate can be readily filtered off and washed. The work will be continued.

---

## LEAD THIOCYANATE.

BY R. D. HALL.

Received March 21, 1908.

NORMAL lead thiocyanate is described by Liebig<sup>1</sup> as a yellow precipitate formed by the action of potassium thiocyanate on lead acetate. The salt, on standing for some time undisturbed, separates as large glistening crystals which are almost insoluble in cold water, but are decomposed by boiling with the formation of a yellow, completely insoluble basic salt. Liebig assigned the formula  $\text{Pb}(\text{CNS})_2$  to the normal salt which formula was established by analysis. The analysis of the basic salt obtained by him is in better agreement with the formula  $\text{PbO} \cdot \text{Pb}(\text{CNS})_2$  than with  $\text{Pb}(\text{OH})(\text{CNS})$ , the formula given in the literature.

In the preparation of lead thiocyanate from pure lead nitrate and potassium thiocyanate, a compound was obtained which differed somewhat from the salt described by Liebig. The crystals were monoclinic like Liebig's but were white and appeared either in large transparent crystals or separated as a feathery mass. Analysis showed these crystals to contain 63.98 per cent. of lead while the formula  $\text{Pb}(\text{CNS})_2$  requires 64.09 per cent. They are completely soluble in hot water and crystallize from solution without suffering decomposition. 3.3 parts of lead thiocyanate dissolve in 100 parts of boiling water, while at 23° C. 0.69 of a part dissolves. Analysis of the recrystallized salt showed 64.03 per cent. of lead.

The crystals were boiled with water for several hours and showed no such decomposition as is described by Liebig, who mentions that under these conditions an insoluble basic salt is formed while at the same time the solution becomes acid. The basic salt can be obtained by the addition of potassium thiocyanate to a solution of basic lead acetate and appears as a white precipitate. The salt prepared in this way shows a lead content of 73.3 per cent. of lead. That required for  $\text{Pb}(\text{OH})(\text{CNS})$  is 73.2 per cent., while the salt obtained by Liebig by the addition of ammonia to a mixture of normal lead acetate and potassium thiocyanate or

<sup>1</sup> Pogg. Ann., 28, 546.

by the decomposition of the normal lead thiocyanate by boiling water, contained 74.96 per cent. of lead, corresponding more nearly to the compound  $\text{PbO.Pb(CNS)}_2$ , which requires 75.7 per cent. of lead. Basic lead thiocyanate is sparingly soluble in boiling water, and crystallizes from hot solutions in small acicular crystals. It is less soluble in water than chloride and more soluble than chromate of lead.

In seeking to ascertain the cause of the yellow discoloration of lead thiocyanate as obtained by Liebig, an investigation was made of the effect of the presence of other salts on the character of the precipitate. It was found that, if the lead solution contains iron, mercury or bismuth salts, the product formed by the addition of potassium thiocyanate is yellow. If a considerable amount of iron is in the solution from which lead thiocyanate is precipitated, the precipitate is yellow with a decided pink cast, while the liquid shows the intense red coloration of ferric thiocyanate. The substance thus obtained, when washed and boiled with water, leaves a residue which resembles ferric hydroxide. When mercuric salts are present in the solution from which lead thiocyanate is obtained, the latter is greenish yellow and is completely soluble in hot water.

The effect of bismuth in the solution has been carefully studied. Basic bismuth thiocyanate was prepared by treating a solution of bismuth oxide in acetic acid with potassium thiocyanate. The white basic salt separates out on heating, while the mother-liquor, when concentrated, yields the finely divided red normal salt. When lead acetate solution contains a small quantity of bismuth acetate, the precipitate which appears by the addition of potassium thiocyanate, comes down slowly and is yellow and crystalline. Analysis of the yellow salt showed 63.8 and 63.95 per cent. of lead, while the normal salt contains 64.09 per cent. While the per cent. of lead is only slightly less than that of the theoretical, the crystals were distinctly yellow, due to the bismuth which they contained. A distinct reaction for bismuth was obtained, after removing the lead as sulphate, by the addition of an alkaline solution of stannous chloride. Moreover all but a very small quantity of the salt dissolved in boiling water. When the solution was filtered, the clear liquid showed an acid reaction and on cooling white crystals appeared. The residue gave a decided reaction for bismuth and

none whatever for lead, showing the bismuth salt to be contained in the lead thiocyanate crystals as impurities which can be removed by crystallization.

Normal solutions of lead nitrate and bismuth nitrate, mixed in various proportions, were precipitated with potassium thiocyanate. The precipitate in each case was filtered, washed rapidly with water, then with alcohol, and dried in an air-bath. The substances thus obtained varied in color from a light yellow to a dark red, depending on the ratio of bismuth to lead in the original solution; the more bismuth the darker was the resulting salt. As nitric acid readily oxidizes lead thiocyanate to sulphate, it is necessary to immediately remove the salt from the liquor by filtration. The precipitates contained varying amounts of bismuth from a trace up to from 6 to 7 per cent. No relation could be determined between the amount of lead thiocyanate and bismuth thiocyanate in the precipitate pointing to the formation of a definite double salt. neither was there any noticeable relation between the amounts of bismuth and lead in the solution to that of bismuth thiocyanate and lead thiocyanate in the precipitate, except the general one that the more bismuth in the solution the more in the precipitate.

A solution which contained 10 cc. of normal bismuth nitrate and 100 cc. of normal lead nitrate gave, with potassium thiocyanate, a precipitate that contained 61.7 per cent. of lead and 2.05 per cent. of bismuth, which is about the proportion of 1 part of bismuth to 30 parts of lead, while the ratio in the solution was 1 part of bismuth to 10 of lead. Where the ratio in the solution was 1 of bismuth to 2 of lead, the salt obtained by the addition of potassium thiocyanate contained 2.8 per cent. of bismuth and 60.8 per cent. of lead, or in about the proportion of 1 part of bismuth to 22 parts of lead. The precipitate from a solution containing five times as much bismuth as lead contained nine times as much lead as bismuth, analysis showing 56.4 per cent. of lead and 6.3 per cent. of bismuth.

Cold water slowly decomposes the yellow salt thus formed, washing away the lead salt and leaving the bismuth. On boiling, all of the lead salt goes into solution leaving a nearly white gelatinous residue, while the liquid becomes acid. Extraction with water does not give a complete separation, as some bismuth is ex-



tracted along with lead. Repeated crystallization will entirely remove the yellow color of the lead thiocyanate. It requires only a trace of bismuth in the solution to give a decided yellow cast to the precipitate, yet a considerable quantity is necessary before enough bismuth is present to appear as a residue when dissolved in boiling water.

Lead thiocyanate is white when pure but is readily contaminated by the presence of foreign salts, especially bismuth, in the solution from which it is precipitated. It is entirely soluble in hot water crystallizing out unchanged on cooling, and can be purified by repeated crystallization. Basic lead thiocyanate can not be prepared by boiling the normal salt with water, but must be prepared from a solution of a basic salt such as the acetate.

UNIVERSITY OF WISCONSIN,  
MADISON, WISCONSIN.

---

[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY,  
No. 63.]

### AMMONIUM VANADICOPHOSPHOTUNGSTATE.

BY EDGAR F. SMITH AND FRANZ F. EXNER.

Received March 26, 1902.

During the summer months of 1901 large quantities of wolframite were examined by us for the purpose of ascertaining just what minute constituents were present in it, which might possibly contaminate the tungstic acid derived from this source. That such impurities existed in tungstic acid seemed very probable as the numerous attempts to fix the atomic weight of tungsten, by reduction of the oxide in hydrogen and subsequent oxidation of the tungsten metal, gave unsatisfactory results. The difference between the maximum and minimum values seemed too great to be attributed entirely to the inefficiency of the method so it was determined to seek for impurities, some hint as to the nature of which it was thought could be best realized by taking into study large quantities of the starting-material—wolframite, from Lawrence County, South Dakota.

The finely divided material was decomposed by prolonged digestion with aqua regia. The hydrated tungstic acid, after filtration and thorough washing, was digested with ammonia water.

This solution gave on evaporation large yields of ammonium paratungstate, which after two or three recrystallizations was perfectly white in color. Portions of the same were ignited to trioxide and the latter digested with a 2 per cent. sodium carbonate solution, after the manner of Taylor,<sup>1</sup> when the white residue observed by him remained. It showed the presence of iron, manganese and tungstic acid. Portions of the same ammonium paratungstate were recrystallized ten times from water, the first portions only being used. The tungsten trioxide from the tenth crystallization, when digested with sodium carbonate, left a white residue in which iron, manganese and tungsten were found as before. This proves that mere crystallization, although repeated many times, fails to eliminate this peculiar compound, noticed by Taylor, which most probably has contaminated all tungstic acid derived from wolframite. It could easily occasion the peculiar rise and fall observed in the many atomic weight determinations made during the last fifty years. We shall, however, refrain from further comment on this point, as the purification of tungstic acid is still under investigation in this laboratory.

Those persons who have made ammonium paratungstate from wolframite have surely noticed the dark color of the mother liquor from the salt. In our work the concentration of the mother liquors was continued until their color was black. The ammonium paratungstate was placed to one side, the mother liquors alone being watched. They became very heavy with increased concentration until finally, after great reduction in volume, greenish yellow masses separated, in which brownish octahedral crystals were found. In the filtrate from the greenish masses additional octahedral forms, now perfectly black in color, separated. The greenish material was removed with difficulty from these crystals. But eventually we discovered that if the dark-colored solutions of the octahedral forms were boiled with pure precipitated calcium carbonate the contaminations of the octahedral substance were entirely eliminated and that the concentrated liquids now yielded brilliant black and quite large octahedra. A half pound of these forms was obtained from the wolframite from Dakota and also from impure ammonium paratungstate made from Connecticut

<sup>1</sup> Thesis for Ph.D., 1901.

wolframite. This compound puzzled us. It showed the presence of ammonia, water and tungstic acid, with a small amount of iron and manganese. That it contained ammonia and tungstic acid and did not give these up when boiled with calcium carbonate, suggested the advisability of boiling aqueous solutions of ammonium paratungstate and ammonium metatungstate with calcium carbonate. The tungstic acid in each case was quantitatively precipitated (or nearly so). Ammonium molybdate also surrendered its molybdic acid content completely to the same reagent.

The question then arose why does not the black, octahedral substance yield its tungstic acid content under similar treatment? Ammonium paratungstate and ammonium metatungstate, when heated with acids, yield tungstic acid. The octahedral compound was boiled for six hours with concentrated hydrochloric acid and three hours more with aqua regia, but tungstic acid did not separate. Evidently the tungstic acid in it was held in a peculiarly combined condition. Boiling with ammonia water caused no change. Fusion with sodium carbonate decomposed the compound. The cold fusion showed a slight bluish tinge, indicating manganese, and on dissolving it in water a slight amount of iron and manganese oxides remained (about 1.20 per cent.). The alkaline aqueous solution, when warmed with hydrochloric acid, gave a precipitate of tungstic acid, which soon acquired a deep orange color. When the black crystals were decomposed with acid potassium sulphate, the cold fusion showed a rosin-like appearance. It dissolved partly in water. The aqueous solution was reddish yellow in color, while the residue was white. The solution, acid in reaction, when acted upon by hydrogen sulphide became amethystine in color; the same coloration was noticed when portions of the solution were saturated with sulphur dioxide. The mystery increased.

A reaction frequently used in this laboratory in the past in the purification of tungstic acid, to expel molybdic acid, was now tried; *viz*: the black crystals were ignited in a crucible, and after reduction to powder, were exposed in a porcelain boat to dry hydrochloric acid gas, when to our amazement a brown-colored liquid appeared in the anterior portion of the tube. On drying, this became greenish blue in color. The acid water in the receiver

showed a faint blue tinge which upon concentration of the solution became more intense, indicating *the presence of vanadium*, which was definitely established by the hydrogen peroxide test as well as by other reactions. Thus, vanadium, a hitherto unsuspected impurity in tungstic acid, was found. But, it might fairly be asked, is it probable that this element exists in ammonium paratungstate? A portion of the latter, perfectly white in color after four recrystallizations from water, was examined and it disclosed vanadium!

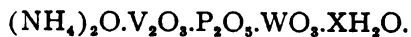
Returning to the black salt it may well be asked why did the sulphuric acid solutions mentioned above take on an amethystine color when they were exposed to the action of hydrogen sulphide and of sulphur dioxide? Surely the presence of small amounts of tungstic acid could not cause this behavior, for ammonium vanadotungstate, prepared according to the recommendation of Dr. Wolcott Gibbs, showed a red or reddish yellow colored solution and gave the blue color characteristic of vanadium when reduced with hydrogen sulphide or sulphur dioxide, after the removal of the major portion of the tungstic acid. How was the peculiar color of the vanadium solution we were studying to be explained? Upon adding ammonium phosphate to ammonium vanadate containing ammonium tungstate, all in aqueous solution, then acidulating with sulphuric acid and reducing the liquid with hydrogen sulphide or sulphur dioxide, an amethystine red color will be produced and not a trace of the blue, always given by vanadium. So at last the abnormal behavior of the latter in the presence of well known reducing agents could be explained. It was due to the presence of phosphoric acid. When some of the black crystals were dissolved in water, and nitric acid and ammonium molybdate added to this solution, the familiar yellow ammonium phosphomolybdate revealed itself.

The puzzle was now solved. The black octahedral salt contained ammonia, water, tungsten, vanadium and phosphorus, with traces of iron and manganese. It was concluded that we had in hand an ammonium phospho-vanado-tungstate. The literature on "complex inorganic acids" gave us no information upon derivatives of this constitution. Assuming that the salt was of this class we employed for its analysis the method of Wolcott Gibbs and also

a method by the same chemist, modified by Friedheim, for vanado-tungstates, but to our surprise both failed, because of the presence of phosphoric acid, so that it was necessary to devise a new method which will be described later elsewhere. It will suffice for the present to mention that success in the analysis was finally reached, and the results are accordingly given as follows:

	Per cent.	Per cent.
(NH <sub>4</sub> ) <sub>2</sub> O.....	5.40	5.27
H <sub>2</sub> O .....	11.85	12.25
WO <sub>3</sub> .....	75.94	75.71
P <sub>2</sub> O <sub>5</sub> .....	0.99	0.94
V <sub>2</sub> O <sub>5</sub> .....	4.03	4.01
Fe <sub>2</sub> O <sub>3</sub> .....	1.19	1.07
MnO .....	0.04	0.05
	<hr/> 99.44	<hr/> 99.30

Ammoniumphospho-vanadates and vanado-tungstates are yellowish red to red in color in aqueous solution. On boiling ammonium tungstate, vanadate and phosphate together, deep red colored solutions resulted. Consequently we were at a loss to account for the brownish black to black color of the aqueous solution of our new salt until after considerable experimenting it was discovered that by the use of vanadium trioxide (V<sub>2</sub>O<sub>5</sub>) with ammonium phosphate and ammonium tungstate black colored solutions were obtained, from which octahedral forms crystallized, containing ammonia, water, tungstic acid, vanadium trioxide and phosphorus pentoxide. Regarding the iron and manganese as adventitious substances and deducting them the percentages of the remaining constituents were about identical with those obtained from a salt which was later prepared as indicated immediately above. The new compound, isolated from the mother-liquors of ammonium paratungstate, is a representative of a new group of derivatives. It may be termed ammonium vanadicophosphotungstate,



It suggested the possibility of forming vanadophosphotungstates, vanadoarsenotungstates, vanadico vanadotungstates, etc., etc. Thirteen such complex bodies have been made and remade. Their analyses are most satisfactory. They will be described later by Mr. Allen Rogers, who is now occupied with their investigation.

It is needless to add that molybdic acid may be substituted for tungstic acid in all these bodies, and very likely columbic and tantallic oxides may be introduced for vanadic, arsenic and phosphoric oxides, and also with them, thus opening up a new and extensive class or group of acids which we hope to study as time permits.

UNIVERSITY OF PENNSYLVANIA.

---

[CONTRIBUTION FROM THE HAVEMEYER LABORATORIES, COLUMBIA UNIVERSITY, No. 62.]

### A NEW QUALITATIVE TEST FOR COBALT.

BY J. L. DANZIGER.

Received March 27, 1902.

THE following test, if carried out properly, will serve to detect the presence of cobalt, in a solution containing 1 part of cobalt, in 500,000 parts of water, provided the solution is colorless or but slightly colored, which can readily be obtained by dilution.

To about 5 cc. of the solution, acid with hydrochloric acid, in a test-tube, there is added solid ammonium thioacetate,  $\text{CH}_3\text{COSNH}_4$ , a few drops of stannous chloride solution, and an equal volume of amyl alcohol, or a mixture of acetone and ether or of alcohol and ether; the whole is well shaken and allowed to separate. If any cobalt is present, the upper layer will be colored blue, the intensity of the color depending on the amount of cobalt present. Solid ammonium thioacetate is added to prevent dilution of the solution, since water destroys the blue color. Stannous chloride is added to reduce any iron present, since ferric iron gives a deep red coloration, as with ammonium thiocyanate. Amyl alcohol, a mixture of acetone and ether or of alcohol and ether, is added to diminish the dissociation and extract the color produced by the undissociated cobalt salt. Amyl alcohol was found to be the most efficient, but is objectionable on account of its disagreeable odor.

In order to ascertain to what compound the color was due, a large amount was prepared by the addition of a saturated solution of ammonium thioacetate to a saturated solution of cobalt chloride, the solution extracted with a mixture of acetone and ether, and the ethereal solution evaporated.

After trying a great number of solvents, it was found impossible to crystallize the substance; so it was washed free from impurities, and its formula deduced from the ratio of cobalt, ammonium, and sulphur present as follows:

About 1 gram of the substance was dissolved in water, an excess of potassium hydroxide added, and the ammonia distilled into a known excess of standard acid, the excess of acid being determined by standard alkali.

The residue in the flask, consisting of cobalt sulphide, potassium sulphide, etc., formed by the decomposing action of the hot strong alkali, was diluted and filtered. The precipitate was treated with a large excess of fuming nitric acid, to oxidize the sulphur, the excess of nitric acid boiled out and the cobalt twice precipitated with potassium hydroxide, dissolved in nitric acid and precipitated as cobalt ammonium phosphate, as described by Dakin<sup>1</sup>, except that alcohol was added to render the precipitation complete, and finally weighed as cobalt pyrophosphate,  $\text{Co}_2\text{P}_2\text{O}_7$ .

The first filtrate from the cobalt, containing sulphides, was oxidized with fuming nitric acid, combined with the other filtrates and the sulphur precipitated as barium sulphate, ignited and weighed.

The analysis was run in duplicate, the results being:

	Gram.	Gram.	Molecular ratios.		Average.
			I.	II.	
$\text{NH}_4$ .....	0.06625	0.07965	1.96	2.03	1.99
S.....	0.23650	0.27970	3.95	4.01	3.98
Co.....	0.11000	0.12866	1.00	1.00	1.00

These ratios approximate 2:4:1, and correspond to the formula  $(\text{CH}_3\text{COS})_2\text{Co} \cdot 2\text{CH}_3\text{COSNH}_4$ .

A number of tests were made to compare the sensitiveness of the test with the thiocyanate test proposed by Vogel<sup>2</sup> and described by Treadwell.<sup>3</sup>

Several solutions of cobalt chloride were prepared, of dilutions varying from 1:5,000 to 1:50,000. To equal amounts of each of these solutions, quantities of ammonium thiocyanate and of ammonium thioacetate, sufficient to saturate them, were added, and

<sup>1</sup> *Chem. News*, Jan. 25, 1901, p. 37.

<sup>2</sup> *Ber. d. chem. Ges.*, 12, 2314 (1879).

<sup>3</sup> *Ztschr. anorg. Chem.*, Jan., 1901, p. 108.

then an equal volume of amyl alcohol. The colors of the upper layers were then compared, and were found to be of equal intensity for each dilution. The thiocyanate test was found to be much more sensitive than Treadwell claimed.

Attention is called to the fact that the double ammonium cobalt thioacetate has 2 molecules of ammonium thioacetate to 1 of cobalt thioacetate; this is analogous to the double ammonium cobalt thiocyanate.

QUANTITATIVE LABORATORY.  
March 11, 1902.

---

## A NOTE ON THE VOLUMETRIC DETERMINATION OF COPPER.

By S. W. PARR.

Received March 31, 1902.

THE volumetric method for copper recently described,<sup>1</sup> wherein the cuprous thiocyanate is titrated directly with permanganate, first in the alkaline and then in the acid condition, is found at times to give an unsatisfactory end reaction. This seems to be due to an incomplete oxidation of the cuprous hydroxide by the permanganate, the latter acting somewhat slowly under the conditions described. Upon acidifying, therefore, any copper remaining in the cuprous condition reverts to the cuprous thiocyanate and in this form is slowly acted upon by the permanganate; hence the occasional indefiniteness at the end.

This difficulty is very easily overcome by the following slight modification: The washed precipitate of cuprous thiocyanate and the asbestos pulp having been returned to the beaker, there is added 10 cc. of a 10 per cent. solution of potassium hydroxide, followed by 10 cc. of ammonia (sp. gr. 0.96) then, without delay, the titration is begun with the standard permanganate solution, continuing until, upon warming, the green color of the supernatant liquid remains. The heating should not be prolonged, 45° to 55° being quite sufficient. Add now a slight excess of permanganate equal to one-third or one-fourth of the quantity needed to produce the permanent green coloration. Allow the mixture to stand for five

<sup>1</sup> This Journal, 22, 685.



minutes, acidify with about 25 cc. of a mixture of concentrated sulphuric acid and water (1 of acid to 1 or 2 of water, cooled to a moderate temperature), and complete the titration to the usual pink coloration. Some heat is developed upon adding the acid to the alkaline solution, but this is without harmful effect. The end reaction is sharp and the results are concordant. The copper in a solution of copper foil was determined electrolytically and also by the above modification with results as follows:

	Electrolytically.	Burette readings.
(a) .....	0.0442	29.3
(b) .....	0.0443	29.3
(c) .....	0.0442	29.3
(d) .....	0.0443	29.25
(e) .....	...	29.2
(f) .....	...	29.3
(g) .....	...	29.3

The iron value of the permanganate multiplied by 0.1602, and the resulting copper factor multiplied by the burette reading 29.3, gives 0.04430 gram of copper as against 0.04425 of electrolytic copper.

To show the concordant nature of the results obtained by this procedure, the readings from the titrations on four ores of widely different character are given as follows:

A.	B.	C.	D.
23.7	10.8	16.2	12.3
23.7	10.8	16.2	12.2

In case of bearing metals, etc., containing both lead and tin, one or the other must be removed because of the formation presumably of lead stannite, which reduces permanganate.

UNIVERSITY OF ILLINOIS.

## THE AMERICAN ELECTROCHEMICAL SOCIETY.

BY JOSEPH W. RICHARDS.

PURSUANT to a call for a meeting signed by C. J. Reed, Carl Hering, E. F. Roeber, W. H. Wahl, of Philadelphia, and J. W. Richards, of Lehigh University, a preliminary meeting to found the above-named society was held at the Engineers' Club, Philadelphia, on November 1, 1901. As the result of that meeting, the

first general meeting of the proposed society was called for April 3d, 4th, and 5th, in Philadelphia, and committees were appointed to enroll members and secure papers.

The meeting for organization was called to order at 8 P.M., April 3rd, in the assembly hall of the Manufacturers' Club, in Philadelphia, with Dr. J. W. Richards in the chair and Carl Hering, secretary *pro tem*. Reports of committees showed that 357 persons had announced themselves for membership, and that 28 papers had been offered for reading at the meeting. The society then organized with title as above, and elected as officers the following:

*President*.—Prof. Joseph W. Richards, Ph.D., Department of Metallurgy, Lehigh University, and Vice-President of The American Chemical Society.

*Vice-Presidents*.—Prof. Charles A. Doremus, College of the City of New York; Prof. H. S. Carhart, University of Michigan; Charles M. Hall, Niagara Falls; Dr. W. D. Bancroft, Cornell University; Dr. Louis Kahlenberg, University of Wisconsin; Dr. W. R. Whitney, Massachusetts Institute of Technology.

*Board of Managers*.—Carl Hering, Dr. E. F. Roeber, Dr. Samuel Sadtler, of Philadelphia; E. G. Atcheson, Niagara Falls; C. O. Mailloux and W. D. Weaver, New York; Edward Weston, Waverly Park, N. J.; Dr. Samuel Sheldon, Brooklyn Institute of Technology; Colonel Samuel Reber, U. S. A., Washington, D. C.

*Treasurer*.—Dr. Pedro G. Salom, The Bourse, Philadelphia.

*Secretary*.—Charles J. Reed, 3313 N. 16th St., Philadelphia.

It was decided to hold two meetings annually and to publish separately the transactions of each meeting. The entrance fee was fixed at five dollars; annual dues five dollars. The next meeting was announced to be held at Niagara Falls the 15th to 18th of September, 1902.

On Friday, April 4th, the society met in the John Harrison Laboratory of Chemistry of the University of Pennsylvania, at 9 A.M., and at the morning session read and discussed the following papers:

A University Course in Electrochemistry, by Joseph W. Richards, Ph.D., Lehigh University.

Graphite Electrodes, by Clarence L. Collins, 2nd, Niagara Falls.

Note on the Gladstone-Tribe Couple, by Prof. W. D. Bancroft, Cornell University.

The Nascent State, by C. J. Reed, Philadelphia.

The Electrolytic Reduction of Lead, by Pedro G. Salom, Ph.D., Philadelphia.

The Refining of Composite Metals, by Titus Ulke, Sault Ste. Marie, Canada.

After lunch in Houston Hall, where the Society was the guest of the University of Pennsylvania, the meeting was resumed in the hall of the new Randal-Morgan Laboratory of Physics, and the following papers were read and discussed:

A Novel Concentration Cell, by Prof. H. S. Carhart, University of Michigan.

The Manufacture of Carbon Bisulphide in the Electric Furnace, by Edward R. Taylor, Penn Yan, N. Y.

Current Electrochemical Theories, by Prof. L. Kahlenberg, University of Wisconsin (read by Prof. C. F. Burgess).

A Zinc-Bromine Storage Battery, by Herbert H. Dow, Midland, Mich.

Continuous Electrolysis of Solutions of Metals, by N. S. Keith, Ph.D., New York City.

A Method of Electrolytic Production of Zinc from its Ores, by Samuel S. Sadtler, Philadelphia.

The Electrolytic Rectifier, by Prof. C. F. Burgess, University of Wisconsin and Carl Hambeuchen, Madison, Wis.

Caustic Alkalies and Chlorine by the Dry Electrolytic Process, by C. E. Acker, Niagara Falls.

On the Relative Speed of the Ions in Solutions of Silver Nitrate in Pyridine and Aceto-Nitrile, by Herman Schlundt, Ph.D., Madison, Wis. (read by Prof. W. D. Bancroft).

On the evening of April 4th, an informal reception was held in the parlors of the Manufacturers' Club, where the members had full opportunity of cultivating each other's personal acquaintance.

On Saturday, April 5th, the sessions were resumed in the John Harrison Laboratory of Chemistry, with reading and discussion of the following:

On a New Type of Electrolytic Meter, by Konrad Norden, Ph.D., New York City.

The Reversible Copper Oxide Plate, by W. McA. Johnson, Hartford, Conn.

A Thermodynamical Note on the Theory of the Edison Battery, by Dr. E. F. Roeber, Philadelphia.

Electrolysis of an Aqueous Solution by Alternating Current, by J. W. Richards, Ph.D., Lehigh University.

The Atom of Electro-Chemistry, by Arvid Reuterdaahl, Providence, R. I.

The papers presented were all freely discussed, and the discussion, being taken down stenographically, will be published with the papers.

On the afternoon of April 3rd, a party of about thirty visited the chemical works of Harrison Bros. & Co., Inc., where various chemical processes were seen, particularly the manufacture of sodium and nitric acid by Darling's process of electrolyzing fused sodium nitrate. On the afternoon of the 5th, over thirty participated in a trip to Bethlehem, Pa., where an hour was spent in the works of the Lehigh Zinc and Iron Co., two hours in the armory and heavy-forging plant of the Bethlehem Steel Co., and a short visit was made to the Lehigh University.

Altogether, nearly 100 members of the new society were in attendance; every paper presented was received attentively and discussed freely, and the membership dispersed, feeling that a move had been made which will react with great energy on the development of the youthful science and industry—that of Electro-chemistry.

---

### NEW BOOKS.

THE LETTERS OF JÖNS JAKOB BERZELIUS AND CHRISTIAN FRIEDERICH SCHÖNBEIN, 1836-1847. Edited by GEORG W. A. KAHLBAUM, Bâle. Translated by FRANCIS V. DARBISHIRE and N. V. SIDGWICK. London: Williams and Norgate. 1900. 112 pp. 12mo. Price, three shillings.

Schönbein, the illustrious discoverer of ozone, gun-cotton and collodion, was a voluminous letter writer; he corresponded with Faraday and other Englishmen, with Eisenlohr of Karlsruhe, Liebig, Pettenkofer, Wöhler, and other eminent German physicists and chemists, with some Swiss, including Marig-

nac. de la Rive and Agassiz, with Henri Sainte Claire Deville and Dumas, in France, as well as with the great Swede Berzelius. Of these letters, numbering more than 1500, two groups have been published by Prof. Georg W. A. Kahlbaum and others, those exchanged with Faraday and those with J. J. Berzelius.

The first six letters of the series in the volume under review refer to the passivity of iron, independently observed, but not discovered by Schönbein, as the phenomena had been described by James Keir as early as 1790. The balance of the correspondence concerns chiefly ozone. In the long letter, dated April 14, 1844, Schönbein writes he has finally decided that the odoriferous principle produced by electrolysis of water, etc., is identical with chlorine, and he gives five reasons for believing this. The fact that ozone is a form of oxygen was suggested to Schönbein on April 20th, in the following year by Plantamour of Geneva.

The discovery of parchment paper is announced in a letter dated March 5, 1846. Three months later Schönbein refers to guncotton as a substance already known, and mentions experimenting with it in small firearms, large guns, and using it for blasting purposes in a tunnel.

This exchange of letters was terminated only by the death of Berzelius in 1848.

Chemists will find this volume an interesting contribution to the history of the science during the period embraced.

HENRY CARRINGTON BOLTON.

A TRAVERS LA MATIÈRE ET L'ÉNERGIE. PAR LE DR. F. E. BLAISE. Paris: Librairie Ch. Delgrave. 1902. 8vo. 344 pp. Prix, broché: 12 fr.

This volume is another example of that strong tendency which is at present manifesting itself on the part of scientific men to write on general philosophical themes. After an introduction covering six pages, the subject matter is treated in six parts, as follows: electrochemistry and mechanics, 122 pp.; matter, 20 pp.; the formation of bodies in space and their luminosity, 8 pp.; electricity, 39 pp.; electrical induction, 102 pp.; philosophical views and conclusions, 34 pp.

The author assumes the existence of a prime ether and then seeks to explain all phenomena as resulting from movements of

the particles of ether. He endeavors to show that the laws of conservation of energy and of matter, as well as all other known laws of chemistry and physics, can be deduced from the basis of his fundamental assumption. He considers atoms as made up of ether particles, and light and electricity as movements of ether. In speaking of organized beings, it is argued that since ether particles unite to form the atoms, the latter are organized and so all matter is organized. Remarks on the application of the laws of electricity and mechanics to the solution of social and moral problems, and on the absolute necessity of the existence of a form of energy capable of intelligence, imagination and volition, form an important portion of part six, which is concluded with a tirade against Darwinism and an attempt to parallel religious dogmas with scientific truths.

The book bears evidence that its author has studied a great variety of subjects; but the relations that he attempts to express are frequently vague and indefinite, and the scientific terms employed are not always correctly used. This appears, for example, in the attempt to explain the relation between Avogadro's hypothesis, Faraday's law, and the law of Dulong and Petit. The energy idea may be said to dominate the book, and yet on page 41 is the statement that according to Faraday's law chemically equivalent quantities of different substances are separated out by the same amount of energy. This clearly shows that the author does not make the very necessary distinction between energy and its factors.

The fundamental assumption that atoms are made up of ether particles is old. And while the author's endeavors to explain diverse well known laws of nature on the basis of this hypothesis are often interesting and suggestive, they are frequently based on further auxiliary assumptions, or are nothing more than mere similitudes. This is strikingly illustrated, for instance, by the comparison of tendencies for good and evil with the action of a mechanical couple and with positive and negative electrical induction. In speaking of Darwinism, surprise is expressed that the conceptions it involves should in this enlightened age have been produced, accepted and perpetuated. Species are considered as unchangeable as atoms themselves—apparently the primal assump-

tion that the latter are composite and consequently not necessarily unchangeable, is overlooked in this connection. Finally the parallelisms between religious dogmas and scientific truths, while in some respects amusing reading, are largely vague, fanciful comparisons, which can hardly be classed as stimulating intellectually or uplifting spiritually.

LOUIS KAHLENBERG.

**SEWAGE AND THE BACTERIAL TREATMENT OF SEWAGE.** BY SAMUEL RIDEAL, D.Sc. (London). Second edition. London: The Sanitary Publishing Co., Ltd. New York: John Wiley & Sons. 1901.

This book is the most comprehensive treatise that has yet appeared on the treatment of sewage. It is so good in a great many respects, that it seems almost ungracious to point out defects, yet in logical arrangement and clearness of statement it leaves much to be desired, and it seems to the reviewer, that though it contains a large amount of most valuable information, and experimental data, it does not give a very clear insight into the practical working of the various processes of sewage treatment. This may be explained by the fact that the book is evidently written from a student's point of view, and the author consequently does not take up the details of construction of plants, nor describe at all fully the practical methods of working the various processes, but rather devotes himself to explaining the changes that the sewage undergoes, and the cause or reason of these changes.

The first five chapters, about one-third of the book, are devoted to the following subjects: Chemical Analyses of Sewage and Effluents, Bacteria Occurring in Sewage, The Changes Produced by Bacteria and Enzymes. Of these chapters, that on chemical analysis is the least interesting, and certain of the methods given, especially that of determining the amount of free ammonia by adding Nessler's solution directly to the sewage, after dilution with water free from ammonia, is open to criticism. The chapters on bacteria, and the changes brought about by bacteria, and enzymes, are well written, but that the reactions as given for the decomposition of carbohydrates and fats, take place in the septic tank, is somewhat doubtful, and in fact it is questionable if any large amount of fat or grease is decomposed in a septic tank.

The remaining chapters of the book are a study of the various processes of sewage treatment: Irrigation and Sewage Farming,

Subsidence and Chemical Precipitation, Sterilization, Contact Beds, Septic Tanks, Continuous Filtration, Agricultural Value of Sewage Effluents, Distribution of Sewage upon Filters, Treatment of Trade Effluents.

These chapters are most interesting reading, being a very full compilation of the results that have been obtained during the past ten years in England. The data they contain is most valuable, but it seems as though too little attention had been paid to the order in which the results are given. Facts relating to the same process are separated from each other, and it is too often necessary to refer to the index to obtain a knowledge of all the data concerning any one process. The only process that has been rather overlooked is Intermittent Filtration, only three pages in all being devoted to the subject. This is to be regretted, as not only was "Intermittent Filtration" the first of the modern bacterial methods, but also the first to show that sewage could be purified on a practical scale by means of bacteria, and it is a method that has, in many places, given excellent results.

It is also to be wished that the author had more often given his personal opinion on the value of the experiments described, for the value of experiments depends on the character of the work, and one has very often to change the opinion formed from reading an account of a process of sewage treatment, after visiting the plant and investigating for himself the methods by which the data were obtained.

A decisive proof, however, of the value of the book taken as a whole, is the fact that it is only a little over a year since the first edition was published, and it can truly be said that it is a book which is essential to every one engaged or interested in the problem of sewage treatment.

LEONARD P. KINNICUTT.

**THE ELEMENTS OF PHYSICAL CHEMISTRY.** BY HARRY C. JONES, Associate Professor of Physical Chemistry in the Johns Hopkins University. New York: The Macmillan Company. 1902. Price, \$4.00.

The importance of physical chemistry, not only as a remarkably fruitful separate branch of science, but also as a most valuable aid in the investigation of problems in many other branches of natural science, such as chemistry proper, physics, geology, biology, physiology, medicine, is now becoming recognized so universally, that



the time may be said to be near or to have already been reached, when no student of science in any one of the above subjects can afford to neglect the study of physical chemistry in his preparation for his future profession. The demand on colleges and universities for adequate instruction in physical chemistry for many classes of students is bound to increase very rapidly. Such a book as the one written by Professor Jones will aid very much in enabling the student to take up the subject with comparatively little difficulty; it presents every side of the subject in a style notably clear and simple; it is sufficiently elementary to form an excellent introduction to physical chemistry and sufficiently thorough, both in the treatment and in its references, to show the student what books and literature he must consult in order to study any particular subject more thoroughly. In this way the book may be said to occupy a place between such other notable works on physical chemistry available for English readers, as Walker's "Introduction to Physical Chemistry," which is somewhat more elementary in character than the present work, and Nernst's "Theoretical Chemistry," and Ostwald's "Outlines of General Chemistry," which are rather more advanced. Professor Jones' book presupposes a knowledge of college physics and chemistry, inorganic and organic; elementary calculus would be necessary in order to follow very closely certain parts of the book, but it is not absolutely essential for an intelligent grasp of the general subject; for a complete mastery of the book and its subject, a knowledge of calculus would be indispensable. The work is designed for students in the later stages of their college work and the earlier part of their university career.

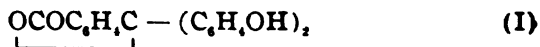
The brief, but carefully prepared, historical sketches introducing many of the chapters, as, for instance, the one on "Chemical Dynamics and Equilibrium," and the great number of references to original papers form excellent features of the book. The marked enthusiasm with which the author writes as a worker in the field, is bound to interest the student in the subject as a living one, with many vital problems yet to be solved. In view of this undeniable gain in stimulating the interest of the intelligent reader, the somewhat disproportionate prominence given the author's own work, considering the general character of the book, may be considered

as pardonable. It is rather surprising, for instance, in glancing over the index as a condensed illustration of this point, to find the name of our greatest American investigator in the realm even of the "new" physical chemistry, J. Willard Gibbs, entirely missing (he is named once, with honor, on page 491); and it is, perhaps, somewhat amusing to find in the same index the author's name referred to about twice as often as van't Hoff's, whereas in Nernst's "Theoretische Chemie" the proportion is as 25 to 1 in favor of the great discoverer of the relations between osmotic pressure and gas pressure. But, as stated, the stimulating effect of the breezy enthusiasm of the author may be said to offset this fault.

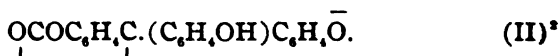
Where much weight is laid—justly—on the extremely important services of the theory of ionization in explaining, qualitatively and quantitatively, in a very simple and beautiful manner any number of otherwise complex phenomena in every field of chemistry, it behooves us, in order to keep the theory above reproach, to be particularly careful not to insist on the adequateness of the theory of ionization in explaining reactions, where experimental facts have been discovered and confirmed that must raise very serious doubts as to the complete correctness of such an explanation. Such a case is Ostwald's beautifully simple theory of indicators.<sup>1</sup>

As the book under discussion, in common with such prominent recent works on physical chemistry as those by Ostwald, Nernst, and Walker, still shows an unquestioning faith in this theory, and no reference to the other side of the problem has been seen in any other text-book, the writer would like to indicate very briefly what the other side is.

According to Ostwald, as is well known, the change of color, in the case of an indicator like phenolphthalein, is ascribed to the change simply from the colorless molecular condition,



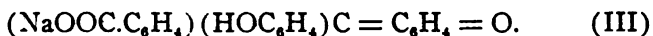
to the red negative ion



<sup>1</sup> Lehrbuch d. allg. Chemie, p. 799 (1891).

<sup>2</sup> Ostwald's "Scientific Foundations of Analytical Chemistry," Jones, p. 260, etc.

Phenolphthaleïn, as a very weak acid, would, indeed, be practically non-ionized in aqueous solution, especially in the presence of even a very small excess of hydrogen ions (from any acid); its alkali salts, undoubtedly would be highly ionized. But nevertheless the change in color is, almost certainly, not due primarily, merely to the change to the ionic condition. As early as 1892, Bernthsen<sup>1</sup> made it appear extremely probable that the color change is really due to a *change of constitution* from the colorless lactoid, form I (with no chromophoric group), to the colored quinoid, form III (with a quinone chromophore),



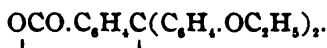
This salt is undoubtedly ionized in solution, but the dry molecular, silver salt is also intensely colored (violet), and the change from the colorless to the colored form of phenolphthaleïn is, therefore, primarily due to a change of constitution. This view is in far better accord with our whole knowledge of color in organic compounds than Ostwald's. The strongest evidence that we have in its favor lies in the fact that Nietzki and Burckhardt<sup>2</sup> have prepared *colored* ethers (non-ionizable) of tetrabromphenolphthaleïn,



and



with quinoid molecules and a *colorless* lactoid ether isomeric with the latter,



A similar explanation applies to most, if not all, other indicators. Writers of books on physical chemistry must take into account such facts as those cited above, and as those established by Hantzsch.<sup>3</sup>

Ostwald's theory, admirable in most of its other details, would be in harmony with such facts, and the known general laws governing color in organic compounds, if sensitiveness to a change, for instance, of constitution, *involving a chromophoric group* under the influence of hydrogen or hydroxyl ions were substituted for sensitiveness merely to a change from a molecular to an ionic condition.

JULIUS STIEGLITZ.

<sup>1</sup> *Chem. Ztg.*, p. 1956 (1892).

<sup>2</sup> *Ber. d. chem. Ges.*, 30, 175 (1897).

<sup>3</sup> *Ibid.*, 32, 575, 3085, 3109 (1899).

**AMERICAN STANDARD SPECIFICATIONS FOR STEEL.** BY ALBERT LADD COLBY. Sold by the writer, South Bethlehem, Pa. Price, \$1.10.

This small book, of 103 pages, contains the revised text of the standard specifications adopted in August, 1901, by the American Section of the International Association for Testing Materials, accompanied by a critical review giving the reasons which governed the committee of the above association in forming its decisions. Since Mr. Colby was himself a member of this committee, the accuracy of the review adds greatly to the value of the work.

The requirements specified are grouped under seven general headings; *viz*: (1) Process of Manufacture; (2) Chemical Properties; (3) Physical Properties; (4) Test Pieces and Methods of Testing; (5) Finish and Variation in Weight; (6) Branding; (7) Inspection. Regarding (1), while the process is specified, the committee omitted restrictions as to the details of the processes, excepting in the case of steel rails. Regarding (2), carbon is omitted where tensile strength is specified, no limit in copper is specified, manganese and silicon are specified in special cases, sulphur in almost all cases, and phosphorus invariably.

Specifications are given for (1) steel castings; (2) axles; (3) forgings; (4) tires; (5) structural steel for buildings; (6) open-hearth boiler plate and rivet steel; (7) rails; (8) splice bars. These serve for the majority of uses to which steel is applied, and modifications may easily be made to suit particular cases.

Regarding chemical analysis, the specifications designate, in the case of each kind of steel, the location from which turnings or drillings are to be taken, but omit all suggestions as to the methods of analysis to be employed.

The book has a business-like appearance, and its contents are the result of so much deliberation by men of the highest qualifications, as to be practically above criticism. The specifications embody the acme of the most recent and most approved practice; their publication and consequent general acceptance as the American standards will save both manufacturers and consumers much misunderstanding, and this little book has hence an important mission to fulfil. The writer is to be congratulated on the satisfactory presentation of the matter which he has made.

J. W. RICHARDS.

**GRUNDZÜGE DER SIDEROLOGIE, ZWEITER THEIL: ZUSAMMENHANG ZWISCHEN THERMISCHER UND MECHANISCHER BEARBEITUNG, KONSTITUTION UND EIGENSCHAFTEN DER EISENLEGIRUNGEN, VON HANNES FREIHERR VON JÜPTNER, Docent an der K. K. Bergakademie in Leoben. Leipzig: Verlag von Arthur Felix. 1901.**

The first volume of this book, which was issued about one and a half years ago, treated of the morphological constituents, and of the physico-chemical ideas as applied to the constitution of iron alloys and slags. With the same care and completeness which characterized the first volume, the author, in the present book, deals with the relations which exist between the heat treatment and work to which iron or steel may be subjected in the process of manufacture, and the physical properties of the finished product. Since the introduction of physico-chemical ideas to the study of iron and steel, especially the idea of considering all alloys as solutions, the growth of the literature on the subject has been extremely rapid. Every person interested in the subject of iron and steel, whether from the point of view of the practical metallurgist or from the purely theoretical side, owes a debt of gratitude to Baron Jüptner for his splendid effort in arranging and systematizing the literature upon this subject. Since the appearance of the first volume, the theoretical knowledge has been so enriched by the applications of the phase rule to the explanation of the equilibrium phenomena, that it has been necessary for the author to give the important work of LeChatelier, Roozeboom, and others, as an introductory chapter in this volume. The book is divided into three parts: I. The influence of heat treatment and work upon the constitution of iron alloys. II. The physical properties of iron alloys in their connection with the chemical composition, the morphological structure, and the thermal and mechanical treatment. III. Relations between constitution, work, and mechanical properties of iron alloys.

In the first part is given a very complete and detailed discussion of Roozeboom's and LeChatelier's application of the phase rule to the study of the constitution of steel. It is extremely interesting to see that such a very practical subject as the steel industry should be receiving so much attention from those interested only in a purely scientific way. There can be no doubt of the fact that the industry will profit by the attention. In this part are also dis-

cussed Roberts-Austen's determinations of the critical points in electrolytic iron; the study of the effect of various elements—carbon, manganese, silicon, etc.—upon the character of the equilibrium curves; the relation between the temperatures of hardening and tempering, and the critical points. The influence of work and heat treatment upon the size of the grain is illustrated by the work of Sauveur on steel rails; and the effect of work above and below the critical range is also discussed. The chapter on segregation contains many interesting facts upon the unequal distribution of the elements among which the author has properly included the occluded gases.

The second part is a compilation of facts in regard to the physical properties of pure iron; specific gravity, melting point, latent heat, thermoelectric behavior, conductivity for electricity and heat, magnetism; and the influence of carbon, manganese, nickel, silicon, etc., on these various properties.

The third part deals with the purely mechanical properties such as tenacity, ductility, elasticity, and hardness and the effect of carbon and other elements upon these properties. Much of the data in Parts II and III are taken from the record of experiments finished before the recent rapid development of microscopic analysis, and consequently there is little relation shown between the properties of particular steels and its microscopic appearance. Future research in these fields will probably demand that the internal structure or morphological constitution be studied in connection with the various physical properties.

Throughout the text, references are always given to the original articles, and at the end of the book under the heading of the three separate parts, is a classified list of authors and their various contributions to the subject.

The book will undoubtedly be read with enthusiasm by all who have anything to do with this very interesting subject. It is to be hoped that the English translation which is under way will be worthy of the original.

HENRY FAY.

**A LABORATORY GUIDE IN ELEMENTARY BACTERIOLOGY.** BY WILLIAM DODGE FROST, M.S. Second Edition. 1902. 348 pp. Published by the author.

This book contains substantially the material furnished by the author to students in bacteriology during two semesters at the University of Wisconsin.

Part I. General Bacteriology (132 pages) includes the elementary technique and direction for the usual systematic study of the biological characteristics of bacteria. Seven types are introduced representing the Saprophilic, Chromogenic, Zymogenic, Saprogenic and Phosphorescent classes of micro-organisms.

Part II. Medical Bacteriology (214 pages) includes the more specialized phases of the subject, particularly as applied to students preparing for medicine.

Outlines are given for the study of one or more forms typical of each of 22 groups, including all of the commonly met with pathogenic organisms.

In both parts of the guide, the forms are taken up in families or groups. An effort is made to have the student recognize the similarity between closely related forms and also to impress him with certain minute but important differences. The sequence of the types is good.

The general plan of the outline for each form is as follows: The organism is introduced with an explanatory note concerning habitat and a list of references to all of the leading English textbooks and occasionally to original sources. Following is an elaborate blank form or chart, covering four pages, for the permanent record, on the part of the student, of the observed morphological, cultural and physiological characteristics of the organism. This outlined chart indicates to the student what is to be done and provides for systematic notes and sketches. Throughout other parts of the book the right-hand pages are left for notes.

The general plan of the guide is good. The material for the fundamental exercises has been carefully selected. The directions for the execution of experiments are explicit and up to date. They bear evidence of having been subjected to class test before publication.

The cuts of apparatus are, for the most part, poorly executed,

and there is also occasional evidence of careless correction of proof.

The appearance of a second edition within a year is the best indication that this elementary laboratory guide fills a need.

ROBERT E. LYONS.

---

## Prize of One Thousand Dollars.

---

The Association for Maintaining the American Women's Table at the Zoological Station at Naples, and for Promoting Scientific Research by Women, hereby announces the offer of a second prize of one thousand dollars, to be awarded in April, 1905, for the best thesis written by a woman, on a scientific subject, embodying new observations and new conclusions based on an independent laboratory research in biological, chemical or physical science.

The conditions of the competition may be learned by application to MRS. ELLEN H. RICHARDS, Massachusetts Institute of Technology, Boston, Mass.



# PROCEEDINGS.

## CONTENTS.

### JANUARY.

Council	(1)
Report of the Committee on Duty-free Importations	(1)
Names Proposed for Membership	(6)
Changes of Address	(8)
Deceased Members	(9)
Meetings of the Sections :	
North Carolina Section	(9)
Notes on Instruction in Dyeing, by G. S. Fraps. Systematic Acid Analysis, by A. S. Wheeler. Recent Work on the Phthaleins, by Charles E. Brewer. A Constant High Temperature Bath, by Charles Baskerville. New Apparatus: (1) Soil Digestion Bath; (2) A Modified Condensing Bulb for Nitrogen Determinations, by C. B. Williams. Nitrification of Ammonium Sulphate and Cottonseed Meal, by W. A. Withers, and G. S. Fraps.	

### FEBRUARY.

Minutes of the Twenty-Fifth General Meeting of the American Chemical Society	(13)
Reports of the Secretary, Treasurer, and Librarian	
Council, Philadelphia Meeting	(24)
Names Proposed for Membership	(28)
New Members Elected January 11, 1902	(28)
Changes of Address	(30)
Board of Directors	(31)
Meetings of the Sections :	
Washington Section	(32)
The British Municipal Laboratories, by H. W. Wiley. Alfred Nobel and the Nobel Prizes, by C. E. Munroe. Experience with Several Methods of Detecting Process Butter, by G. E. Patrick. The Solubility of Mixtures of Sodium Chloride and Sodium Sulphate, by A. Seidell. The Evolution of Metallic Retorts, by W. H. Seaman. Starch as an Adulterant or Dryer in Butter, and a Study of Glucose in Butters, by G. E. Patrick and D. Stuart.	
Columbus Section	(36)

### MARCH.

Council	(37)
Names Proposed for Membership	(37)
New Members Elected February 8, 1902	(38)
New Members Elected February 22, 1902	(39)
Changes of Address	(40)
Meetings of the Sections :	
Washington Section	(40)

(IV)

**Kansas City Section . . . . . (41)**

Methods of Classification of Mineral Waters, by E. H. S. Bailey. Cottonseed Oil and Its Uses in Commerce, by P. F. Nishkian. Food Preservatives: Their Use, Abuse, and Toxicology, by J. R. Moechel. The Manufacture and Chemistry of Portland Cement, by E. C. Champion.

**APRIL.**

Names Proposed for Membership . . . . .	(45)
New Members Elected March 10, 1902 . . . . .	(45)
Changes of Address . . . . .	(45)

**MAY.**

Names Proposed for Membership . . . . .	(47)
New Members Elected March 29, 1902 . . . . .	(47)
Changes of Address . . . . .	(48)
Deceased Members . . . . .	(49)
Meetings of the Sections:	

**Michigan Section . . . . . (49)**

Michigan as a Beet-Sugar State, by P. F. Trowbridge. Solubility of Calcium Carbonate in Water Free from Carbon Dioxide, by H. E. Brown. Solubility, by G. A. Hulett. The Volumetric Estimation of Alumina and Free and Combined Sulphuric Acid in Alums, by A. H. White.

**Washington Section . . . . . (50)**

Common Errors in the Determination of Silica, by W. F. Hillebrand. Researches on the Oxides of Tungsten, by E. T. Allen.

**JUNE.**

Names Proposed for Membership . . . . .	(51)
New Members Elected April 17, 1902 . . . . .	(52)
Changes of Address . . . . .	(52)
Deceased Members; Obituary of Alfred Ripley Leeds . . . . .	(53)
Meetings of the Sections:	

**Chicago Section . . . . . (58)**

The Electrochemical Industries of Niagara Falls, by C. F. Chandler. Coals of Illinois and Their Calorific Determination, by S. W. Parr. Practical Water Softening, by C. L. Kennicott. Manufacture and Analysis of Alloys, by A. Thurnauer. Borax, by S. T. Mather.

**New York Section; The Nichols Medal . . . . . (58)**

**JULY.**

Board of Directors . . . . .	(61)
Names Proposed for Membership . . . . .	(62)
New Members Elected May 22, 1902 . . . . .	(63)
New Members Elected June 23, 1902 . . . . .	(63)
Changes of Address . . . . .	(64)
Meetings of the Sections:	

**North Carolina Section . . . . . (66)**

Molecular Attraction, by J. E. Mills. Bromination of Heptane under Pressure, by A. S. Wheeler. Notes on the Occurrence of Cobalt in Wake County, N. C., by S. E. Asbury. Action of Chloral on the Nitrazilines, by A. S. Wheeler and H. R. Weller. The Determination of Starch in

(V)

Baking Powders, by W. M. Allen. Arsenic Pentachloride, by Charles Baskerville and H. H. Bennett. Separation of Pure Praseodymium Compounds, by Charles Baskerville and J. W. Turrentine. The Sulphur Content of Some Plants, by G. S. Fraps. Determination of Sulphuric Acid in Soils, by C. B. Williams. Some New Reactions of Thorium and Allied Elements with Organic Bases, by Charles Baskerville and F. H. Lemly. Rediscovery of a Process for Rendering Phosphoric Acid Available, by Charles Baskerville. A Platinum Air-bath by Charles Baskerville. Black Rain in North Carolina, by Charles Baskerville and H. R. Weller.

Michigan Section . . . . . (67)

Chemical Architecture, by J. M. Francis. Comparison of Methods for Direct Analysis of Beets, by D. L. Davoll, Jr. Trivalent Carbon, by M. Gomberg.

**AUGUST.**

Twenty-Sixth General Meeting of the American Chemical Society . . . . . (69)

Council . . . . . (70)

Names Proposed for Membership . . . . . (73)

New Members Elected July 14, 1902 . . . . . (73)

Changes of Address . . . . . (74)

**SEPTEMBER.**

Council . . . . . (77)

Names Proposed for Membership . . . . . (77)

New Members Elected August 7 and August 21, 1902 . . . . . (78)

Changes of Address . . . . . (78)

Deceased Member . . . . . (79)

Meetings of the Sections :

Cincinnati Section . . . . . (79)

The Influence of Salts on the Miscibility of Liquids, by J. F. Snell. On the Relation of the Heat of Combustion to the Specific Gravity of Fatty Oils, by H. G. Sherman and J. F. Snell. On the Determination of Essential Oils, by L. L. Watters. Some Curious Mineral and Geological Specimens from Kentucky, by J. U. Lloyd. Derivatives of Tetrahydroquinoline, by Thomas Evans. Sulphur in Cottonseed, by T. D. Winterstroem. Remarks on Infectious Diseases, by Alfred Springer. Magnesium Amalgam as a Reducing Agent, by H. S. Fry. Report on Knietach's Paper on the Manufacture of Sulphuric Acid by the Contact Process, by J. F. Snell. Systems of Water Purification, by J. W. Kilma. Review of Grignard's Paper on Magnesium Organic Compounds, by Thomas Evans. On the Adulteration of Lavender Oil with Salicylic Acid, by Everhard Weber. Meta- and Anabromtetrahydroquinoline, by Geoffrey A. Gray. A By-product of the Alkaline Bromination of Cinnamic Acid, by Lloyd A. Meader.

**OCTOBER.**

Names Proposed for Membership . . . . . (81)

New Members Elected September 26, 1902 . . . . . (81)

Changes of Address . . . . . (82)

Deceased Member . . . . . (83)

Meetings of the Sections :

(VI)

Philadelphia Section . . . . . (84)

Some Phases of Textile Chemistry, by J. M. Matthews. The Relation of Chemistry to the National Government, by H. W. Wiley. The Steel Works Laboratory, by G. W. Sargent. Carbon by Combustion, by George Auchy.

Kansas City Section . . . . . (84)

The Manufacture and Chemistry of Portland Cement, by E. C. Champion. The Manufacture and Chemistry of Fertilizers, by J. M. Barrett. Some Alkaloids and Their Synthetical Preparation and Some Derivatives of Quinoline, by Edward Bartow. Liquid Air, by E. C. Franklin. Colloidal Solutions, by L. I. Blake.

NOVEMBER.

Council : Amendment to the Constitution . . . . . (85)

New Members Elected from September 26 to October 27, 1902 . . . . . (86)

Changes of Address . . . . . (88)

Meetings of the Sections :

Chicago Section . . . . . (90)

What Can the Chemist Do to Conserve Public Health, by H. W. Wiley.

DECEMBER.

Fifth International Congress of Applied Chemistry . . . . . (91)

Board of Directors . . . . . (94)

Council . . . . . (95)

Members Elected between October 28 and November 27, 1902 . . . . . (95)

Changes of Address . . . . . (97)

Addresses Wanted . . . . . (99)

Meetings of the Sections :

North Carolina Section . . . . . (99)

Some New Double Sulphates of Lanthanum, and on the Existence of Lanthanum Alumina, by Charles Baskerville and E. G. Moss. Lanthanates, by Charles Baskerville and G. F. Catlett. Studies in Nitrification, by G. S. Fraps. Improved Method for the Determination of Halogens in Atomic Weight Work, by Charles Baskerville and R. O. E. Davis. Chlorides in Tobacco, by W. H. Pegram. Suggested Change in the Law of Dulong and Petit, by J. E. Mills. Neodymates, by Charles Baskerville and W. O. Heard. Artificial Plant Food Requirements of Soils, by B. W. Kilgore. Methods for the Determination of Total Phosphoric Acid and Potash in Soils, by C. B. Williams.

New York Section . . . . . (100)

Oxychloride of Magnesium and Its Industrial Uses, by Leo Baekeland. Some New Photographic Chemicals; read by Mr. Bugg. The Determination of Sulphur and Phosphorus in Organic Materials by H. C. Sherman. The Composition of Cows' Milk, by H. C. Sherman. The Occurrence of Salicylic Acid in Fruits, by F. W. Traphagen and Edmund Burke; read by Professor M. T. Bogert.

Deceased Members . . . . . (100)

## Proceedings.

### COUNCIL.

#### REPORT OF THE COMMITTEE ON DUTY-FREE IMPORTATIONS.<sup>1</sup>

*To the Council of the American Chemical Society:*

GENTLEMEN:—For a number of years some of our schools have had no little trouble in the matter of duty-free importation of chemicals and apparatus in bond from foreign countries. This question has become of interest to the American Chemical Society, and ten years ago a committee was appointed to investigate complaints and seek a remedy for the annoyance. During several years following the appointment of this committee the assessment of duties against colleges for certain articles imported in bond decreased materially and it was thought almost unnecessary to continue the committee. But about three years ago the pernicious activity of certain customs officials, acting on their own authority apparently, began to be again felt and renewed complaints were heard of duties demanded from scientific institutions on articles imported for instruction work only. The subject was, therefore, taken up anew by the committee and through the chairman, Prof. Charles E. Munroe, a lengthy report was made at the Chicago meeting, of last winter, and was published in the February, 1901, number of the Journal. This report explains thoroughly the origin of the present law and quotes a number of decisions bearing on the interpretation of the law. It was learned that the rulings of collectors in the different ports of entry in the country are quite arbitrary, from which it follows that while some colleges are generally taxed others are permitted to import everything required duty-free. In order to discover the extent of this discrimination it was thought best to collect information from the leading institutions of the country and learn, if possible, the ground for the discrimination. At the request of Professor Munroe the present writer took the matter in hand and began by addressing a circular letter to some officer of each one of

<sup>1</sup> Presented at the Denver meeting of the American Chemical Society.

(2)

the larger schools. In most cases a reply was received to the circular and from these answers the following table was compiled, which presents the important facts discovered. The letter of inquiry is also given :

NORTHWESTERN UNIVERSITY LABORATORIES,  
2421 Dearborn St., Chicago.

DEAR SIR :

I call your attention to the "Report of the Committee on Duty-free Importations" reprinted from the Journal of the American Chemical Society, February number, 1901, and sent under separate cover, and refer you to page 43. The abuse of the original intention of the law permitting colleges to import apparatus and chemicals free of duty has grown to be a serious matter for some schools, and should be corrected.

The assessment of duty is not uniform and seems to depend on the personal interpretation of the law by the individual Collector of Customs at each port of entry. Many of our schools have never been called upon to pay duty on articles imported, while other schools have been obliged to pay on a number of articles in the last ten years. I am anxious to secure full data on this subject from which to form a report to be presented at the next meeting of the American Chemical Society. To aid in this will you kindly answer the following questions :

1. Through which port of entry do you usually obtain your foreign chemicals and apparatus?
2. Have you been obliged to pay duty in recent years, and, if so, on what articles?

It is believed that a proper presentation of the facts, brought out by this inquiry, to the secretary of the treasury, will have the desired result of correcting the unjust tax and discrimination. If you are not directly concerned with the importation of articles for your institution, will you kindly hand this letter to the member of your faculty who has the matter in charge.

Yours truly,  
J. H. LONG.

Name of College.	Port of entry for goods.	
Western University of Pennsylvania.	New York.	No duties paid.
Washington and Lee.		Duty paid on glassware, thermometers, rubber tubing and rubber stoppers.
College of City of New York.	New York.	No duties paid.
Columbian University.	Georgetown.	No duties paid.
Case School of Applied Science.		No duties paid.
Wesleyan University.	New York.	Paid duty on paper scale thermometers.
Amherst.	New York.	No duties paid.
University of Minnesota.	Minneapolis.	This institution has recently been charged over \$1,200.00 duty on articles imported for the department of chemistry alone. Porcelain dishes were taxed as "plain earthenware;" crucibles as "decorated earthenware." Equally absurd rulings were made on other items. In former years importations were made through other ports of entry and were never taxed.
Philadelphia College of Pharmacy.	Philadelphia.	No duties paid.
DePauw University.	New York.	No duties paid.
Columbia.	New York.	Hessian crucibles and Anschütz thermometers standardized by the Reichsanstalt were taxed recently.
Stanford.	San Francisco.	No duties paid.
Harvard.	Boston.	Duties have been assessed on various small articles.
University of California.	San Francisco.	No duties have been paid.
Ohio State University.	New York.	No duties of consequence have been paid.

Name of College. University of Virginia, Johns Hopkins,	Port of entry for goods. New York. Baltimore.	
	Duties have been paid on a few small items.	
	Duties have been assessed for several years. Last year 45 per cent. ad valorem was charged on brass gauze in squares, magnets, pinch-cocks, zinc dust, lead crucibles, and squares of French plate-glass. On glass-stoppered bottles, plain and labeled, the charge was 40 per cent. All funnels were classed as blown glass and a duty of 60 per cent. was charged. Porcelain evaporating dishes and mortars were classed as white earthenware and a duty of 55 per cent. charged. On the following chemicals a duty of 25 per cent. was charged: Cadmium sulphate, cobalt chloride, cobalt sulphate, potassium permanganate, potassium iodide, potassium bromide, mercury cyanide, and iodine. On potassium cyanide 12 1/2 per cent. was charged, and on oxalic acid 7 cents per pound.	
Ann Arbor.	{ New York. Philadelphia. Detroit.	On goods obtained recently through New York, costing in Germany, 1100 marks, a duty of \$78.85 was paid. The articles taxed were funnels, bottles, flasks, thermometers, stop-cocks, glass joints and water-blasts. Duty amounting to \$7.65 was paid on an invoice of apparatus used in physical chemistry. A tax of \$76.00 was paid on an invoice of apparatus for physical chemistry worth \$500, imported through Detroit. On certain pieces of apparatus in this lot the metal parts were separately packed and were assessed, while the glass parts, packed by themselves, were allowed free entry. On goods received through Philadelphia no duty has been paid.
University of Pennsylvania.	Philadelphia.	Duties have been paid on filter-paper and a few other items.



Name of College.	Port of entry for goods.	
Cornell.	New York.	Duties have been paid on etched glassware and absolute alcohol.
Northwestern.	Chicago.	Duties have been paid on filter-paper and several small items.
University of Chicago.	{ Chicago.	Duty has been assessed recently on numerous articles, among which are graphite rheostats, wire rheostats, ordinary thermometers, Anschütz thermometers, standard thermometers, glass tubing, blast-lamps, foot-blowers, blowpipe charcoal, charcoal sticks for cutting glass, clay plates for furnaces, rubber tubing, scientific lantern slides, sodium press, etc.
	{ New York.	
New Hampshire College.	New York.	No duty has been assessed.
University of Iowa.	New York.	Duties have been charged on filter-paper and thermometers.
Rose Polytechnic Institute.	New York.	Duties have been charged on thermometers and common balances.
Massachusetts Inst. of Technology.	{ Boston.	Duty has been assessed on bottles only, imported through New York.
	{ New York.	
University of North Carolina.	{ New York.	No duties have been paid.
University of Nebraska.	{ Philadelphia.	No duties have been paid.
Yale.	Lincoln.	No duties have been paid recently.
Worcester Polytechnic Institute.	New York.	No duties have been paid.
University of Kansas.	Kansas City.	Duty has been assessed on thermometers, porcelain mortars, and on Ostwald thermostats.
University of Wisconsin.	New York.	Duty has been charged on thermometers and rubber tubing.
Purdue.	New York.	Duty has been charged on filter-paper and a set of weights.
Rensselaer Polytechnic Institute.	New York.	No duty has been charged recently.
Brown University.	New York.	No duties charged.
Michigan Agricultural College.	New York.	No duty has been charged recently.

The statement made above, that the assessment of duty appears to be purely arbitrary, depending on the opinion of an individual collector or appraiser, is fully confirmed by the data of the table. Some collectors have attempted to justify their rulings by the plea that only such articles are taxed as are commonly used in trade or technology. But it is hard to see how Ostwald thermostats, sodium presses or Anschütz thermometers, standardized at the Reichsanstalt, can be brought under this classification. It is also singular that many schools are able to report that they have never been obliged to pay duty. Contrast this with the excess of zeal displayed by the collectors at Baltimore and Minneapolis, and the complete absurdity of the present interpretation of the law becomes apparent. With such facts at hand the American Chemical Society is now ready to present the matter to the secretary of the treasury, and ask for such authoritative and final rulings as will put an end to the annoyance at once and for good.

Respectfully submitted,

J. H. LONG.

#### NAMES PROPOSED FOR MEMBERSHIP.

- Abbott, Francis L., Eveleth, Minn.  
 Andrews, Clement W., The John Crerar Library, Chicago, Ill.  
 Ashbrook, Donald S., 3614 Baring St., Philadelphia, Pa.  
 Blaisdell, Albert C., N. Woburn, Mass.  
 Bowen, John R., Tarentum, Pa.  
 Breazele, J. F., Bureau of Soils, Dept. of Agr., Washington, D. C.  
 Brown, Bailey E., Bureau of Soils, Dept. of Agr., Washington, D. C.  
 Burd, John S., Bureau of Chemistry, Department of Agr., Washington, D. C.  
 Clark, Friend E., Johns Hopkins Univ., Baltimore, Md.  
 Cox, Alvin J., Stanford University, Cal.  
 Dunlap, Eugene E., 2016 N. 11th St., Philadelphia, Pa.  
 Easton, Wm. H., 224 S. 43rd St., Philadelphia, Pa.  
 Emery, William O., Crawfordsville, Ind.  
 Eyles, Arthur H., Addingham, Pa.  
 Fernberger, Harry M., 43 Central Ave., Waterbury, Conn.  
 Fischer, Richard, Madison, Wis.  
 Folin, Otto, McLean Hospital, Waverley, Mass.  
 Fulweiler, Walter H., 4121 Girard Ave., Philadelphia, Pa.  
 Gatchel, Joshua L., 47 Avenue C, Bayonne, N. J.  
 Gillman, Robert G., State Normal School, Terre Haute, Ind.

- Graham, J. Howard, 2108 N. Marshall St., Philadelphia, Pa.  
 Haas, Harry L., 526-530 W. 25th St., N. Y. City.  
 Harcourt, R., Ontario Agr. Coll., Guelph, Ontario.  
 Haslwanter, Charles, 904 Flushing Ave., Brooklyn, N. Y.  
 Hayes, Edgar B., care S. and S. Packing Co., Kansas City,  
 Kans.  
 Hopkins, Matthew S. Roylton, cor. North and Maryland Ave.,  
 Baltimore, Md.  
 Hunter, H. B., S. E. Cor. 36th St. and First Ave., N. Y. City.  
 Kammerer, Alfred L., 391 Dormitories, Univ. of Pa., Phila-  
 delphia, Pa.  
 Kauffman, Warren L., Box 2, Yonkers, N. Y.  
 Kollock, (Miss) Lily G., 1926 Spring Garden St., Philadel-  
 phia, Pa.  
 Lewis, Frederick H., Craigsville, Va.  
 Lord, E. C. E., 1910 I St., Washington, D. C.  
 Lowenstein, Arthur, 2538 Moorman Ave., Walnut Hills, Cin-  
 cinnati, O.  
 Marsh, Harry B., Penn. Mil. Coll., Chester, Pa.  
 Masson, Victor E., Hammondsport, Steuben Co., N. Y.  
 Matthews, Charles R., 3313 Prytania St., New Orleans, La.  
 McCoy, Herbert N., Kent Chem. Lab., Univ. of Chicago, Chi-  
 cago, Ill.  
 McKee, Ralph H., Lake Forest, Ill.  
 Moerk, Frank X., 145 N. 10th St., Philadelphia, Pa.  
 Monfort, W. F., Marietta, O.  
 Montgomery, Thomas S., 39th and Baring Sts., W. Philadelphia,  
 Pa.  
 Newkirk, C. C., 614 W. 9th St., Cincinnati, O.  
 Pate, W. F., Urbana, Ill.  
 Ransom, J. H., 125 S. Grant St., W. Lafayette, Ind.  
 Seeler, Felix, care of Geo. Lueders and Co., Elizabeth, N. J.  
 Smith, Carl E., 1700 Fitzwater St., Philadelphia, Pa.  
 Smith, Frank R., Wilmington, Del.  
 Smith, Roy B., Colgate Univ., Hamilton, N. Y.  
 Spayd, Charles H., 48 N. 51st St., Philadelphia, Pa.  
 Taite, Samuel S., 4708 Windsor Ave., W. Philadelphia, Pa.  
 Talbot, (Miss) Marion, University of Chicago, Chicago, Ill.  
 Thompson, Kirk W., 4 Burton Ave., Beverly, Mass.  
 Tolley, Thomas W., Tuskegee, Ala.  
 VanArsdale, G. D., Room 68, 99 John St., N. Y. City.  
 Vorce, LaFayette D., 5225 Madison Ave., Chicago, Ill.  
 Wahlenberg, John A., care Orford Copper Co., New Brighton,  
 N. Y.  
 Warfel, R. R., Allegheny Steel and Iron Co., Avenue, Pa.  
 Weston, Berne F., Monessen, Pa.  
 Whittelsey, Theodore, Ithaca, N. Y.  
 Wyman, Levi P., 1350 S. 46th St., Philadelphia, Pa.

# NAMES PROPOSED FOR ASSOCIATE MEMBERSHIP.

Johnston, Richard H., 972 Park Place, Brooklyn, N. Y.  
 Stuart, (Miss) Emma L., 5485 Hays St., Pittsburg, Pa.

## CHANGES OF ADDRESS.

Annear, John B., 1052 Regent St., Boulder, Colo.  
 Argall, Philip H., Univ. of Colo., Boulder, Colo.  
 Arnott, G. W. Campbell, 12 Richmond St., E., Toronto, Ontario.  
 Atwood, Frank W., 216 Milk St., Boston, Mass.  
 Bigelow, S. Lawrence, 1520 Hill St., Ann Arbor, Mich.  
 Bizzell, James A., 45 East Avenue, Ithaca, N. Y.  
 Blouin, R. E., Audubon Park, New Orleans, La.  
 Browne, C. A., Jr., State College, Pa.  
 Carveth, H. R., 115 Cook St., Ithaca, N. Y.  
 Campbell, E. D., 1555 Washtenaw Ave., Ann Arbor, Mich.  
 Cayvan, L. L., 322 W. Monroe St., Chicago, Ill.  
 Closson, C. D., 1329 Sacramento St., Columbus, Ohio.  
 Cushman, Allerton S., U. S. Dept. Agr., Washington, D. C.  
 Dales, Benton, 115 Cook St., Ithaca, N. Y.  
 Danziger, J. L., 302 W. 114th St., New York City.  
 Darke, Jesse M., 351 Essex St., Lynn, Mass.  
 Desper, Ernest W., 16 Kendall St., Worcester, Mass.  
 Diehl, O. C., Box 337, Saginaw, Mich.  
 Dorr, John V. N., Deadwood, S. D.  
 Dreyfus, W. E., 500 W. 123d St., N. Y. City.  
 Earle, Richard B., 15 Hollis Hall, Cambridge, Mass.  
 Fassett, Charles M., 702 Main Ave., Spokane, Wash.  
 Fosdick, E. H., 828 East 3rd St., Los Angeles, Cal.  
 Gass, James K., 413 Van Hock St., Camden, N. J.  
 Geisler, Joseph F., New York Mercantile Exchange, N. Y. City.  
 Getman, F. H., Johns Hopkins Univ., Baltimore, Md.  
 Getz, W. H., 2704 Locust St., St. Louis, Mo.  
 Griffith, S. H., 1308 New Hampshire Ave., Washington, D. C.  
 Hildreth, T. F., Pittsburg Steel Foundry, Glassport, Pa.  
 Hancock, W. J., 147 Remsen St., Brooklyn, N. Y.  
 Harris, Isaac F., Box 43, New Haven, Conn.  
 Hendee, Edward T., N. Y. Univ., University Heights, N. Y.  
 Hillyer, Wm. E., The Chesapeake and Potomac Telephone Co.,  
 619 14th St., N. W., Washington, D. C.  
 Hopkins, N. M., 1833 Kalorama Ave., Washington, D. C.  
 Jones, W. J., Jr., Chief Deputy State Chemist, Lafayette, Ind.  
 Krebs, A. Sonnin, care Krebs Pigment and Chemical Co.,  
 Newport, Del.  
 Lanning, John G., 106 Miles Ave., Cleveland, O.  
 Laist, Frederick, 1408 N. Main St., Santa Ana, Cal.  
 Labonde, Leon, Box 594, Rochester, N. Y.

- Loub, Charles M., 19 Liberty St., N. Y. City.  
 Mackay, P. A., care of Wenona Zinc Mfg. Co., Wenona, Ill.  
 Merzbacher, Aaron, Laboratory of Reading Iron Co., Reading, Pa.  
 Mixer, Charles T., Salt Lake City, Utah.  
 Moale, Philip R., Secy.-Treas. Asheville Ptg. Co., Asheville, N. C.  
 Mommers, Richard, care Glucose Sugar Ref. Co., Taylor and Beach Sts., Chicago.  
 Moody, Herbert R., 616 Main St., Geneva, N. Y.  
 Murrill, Paul, Middletown, Conn.  
 Parker, H. N., care of Board of Health, 456 Bloomfield Ave., Montclair, N. J.  
 Peppel, S. V., Ohio Geol. Survey, Columbus, O.  
 Perkins, George E., 5 Adie St., Providence, R. I.  
 Perkins, T. S., 318 California St., San Francisco, Cal.  
 Phalen, W. C., 305 Broadway, Cambridge, Mass.  
 Porter, J. L., 602 Carondelet St., New Orleans, La.  
 Rademacher, H. A., care Law Office of Pierson and Pease, Chamber of Commerce, Chicago.  
 Rauchfuss, Eugene J., 36th St., and 1st Ave., N. Y. City.  
 Rosentwist, B. G. A., Hyde Park, Mass.  
 Smith, Edward S., 219 E. Market St., Warren, Ohio.  
 Smith, H. Monmouth, 701 University Ave., Syracuse, N. Y.  
 Strahorn, A. T., North Platte, Nebr.  
 Takamine, Jokichi, 61 W. 108th St., N. Y. City.  
 Thompson, G. W., 129 York St., Brooklyn, N. Y.  
 Thorburn, A. D., 55 Walnut St., Chicago, Ill.  
 Voorhees, Louis A., Box 357, New Brunswick, N. J.  
 Van der Linde, Harold T. G., Gutta Percha and Rubber Mfg. Co., 47-50 Front St., W., Toronto, Canada.  
 Whitehead, Robert L., Seattle S. & R. Co., Seattle, Wash.

---

#### DECEASED MEMBER.

William Van Slooten, of Brooklyn, N. Y., member of the Society since 1898, died December 14, 1901.

---

### MEETINGS OF THE SECTIONS.

#### NORTH CAROLINA SECTION.

The fall meeting of the North Carolina Section was held on Saturday, November 23, 1901, at 11 A.M. in the office of the state chemist, Agricultural Building, Raleigh, with Presiding Officer W. A. Withers in the chair. Eighteen (18) members and visitors participated in the meeting.

After the reading and adoption of the minutes of the previous meeting and the transaction of some minor miscellaneous business, the following program was presented and discussed :

"Notes on Instruction in Dyeing," by G. S. Fraps.

The author gave a brief account of methods used and results obtained, in teaching dyeing at the North Carolina College of Agriculture and Mechanic Arts. Scrap books, which had been prepared by students, containing dyed samples and tests made on them were exhibited, to show the methods pursued.

"Systematic Acid Analysis," by A. S. Wheeler.

The plan suggested by Abegg and Herz (*Ztschr. anorg. Chem.*, 23, 236) is being tried with certain modifications with his classes in qualitative analysis in the University of North Carolina with considerable success. He finds it to be the nearest approach to a separation similar to that used with bases that he has cognizance of.

"Recent Work on the Phthaleins," by Charles E. Brewer.

This was a review of several articles that have recently appeared. The first of these was by Orndorff and Brewer on the constitution of gallein. The other three articles, in the current volume of the *Berichte*, contributed by Liebermann, Thiele and Jaeger, and Feuerstein and Dutoit, were on dioxyfluorescein or oxhydroquinone phthalein. In every case the view that the phthaleins react as tautomeric compounds was sustained. All the contributors agree that those derivations which have color should be given the quinoid structure, while those which are colorless are properly represented by the lactoid structure. A number of the compounds belonging to each of these two classes were reported.

"A Constant High Temperature Bath," by Charles Baskerville.

An ordinary enameled iron water-bath is made use of, surrounded by asbestos with a copper cover and a second asbestos top projecting in the bath and a wrought iron float constructed to hold crucibles of various sizes. The liquid of the bath is composed of a mixture of the more fusible alloys. A specially constructed thermostat, made of very infusible glass, controls the flame of a large lamp. A glass tube, open at the bottom, penetrates the dual cover and is placed within one of the crucible receptacles. A mercury thermometer under 20° atmospheric pressure is used.

"New Apparatus: (1) Soil Digestion Bath; and (2) A Modified Condensing Bulb Tube for Nitrogen Determinations," by C. B. Williams.

Drawings of these two pieces of apparatus, designed for use in

the chemical laboratory of the North Carolina Department of Agriculture, were submitted ; also a description was read. Mr. Williams stated that these two pieces of apparatus had proved very valuable to him in his work, both in point of economy of time and reliability.

“ Nitrification of Ammonium Sulphate and Cottonseed Meal,”  
by W. A. Withers and G. S. Fraps.

The conclusions drawn by the authors from their pot experiments on nitrification are :

- a.* Ammonium sulphate in some cases hinders nitrification.
- b.* In nitrification of ammonium sulphate, sulphuric acid is produced and hinders the process unless neutralized.
- c.* Soils differ in their action, depending upon the kinds of bacteria present.
- d.* The relative number of organisms in the soil capable of nitrifying ammonium sulphate may be increased by continued addition of the substance and lime if such germs were originally present.
- e.* Calcium carbonate is very helpful in nitrification.

CHARLES BURGESS WILLIAMS, *Secretary.*





## Proceedings.

### MINUTES OF THE TWENTY-FIFTH GENERAL MEETING OF THE AMERICAN CHEMICAL SOCIETY.

The Twenty-Fifth General Meeting of the American Chemical Society was called to order in Houston Hall, University of Pennsylvania, at 9.45 A.M., December 30, 1901. Addresses of welcome were presented by Dr. J. Merritt Matthews, chairman of the Philadelphia Section; Honorable Samuel H. Ashbridge, mayor of Philadelphia; and Professor Edgar F. Smith, vice-provost of the University of Pennsylvania; President F. W. Clarke responded on behalf of the American Chemical Society.

After the introductory exercises, the minutes of the previous meetings of the Society were adopted, as already printed in the Journal, and the report of the secretary was presented and accepted.

The secretary also presented the report of the librarian, which was accepted. President F. W. Clarke then made a brief oral report, as chairman of the Committee on Atomic Weights, and as chairman of the International Committee on Atomic Weights.

Communications were presented by the secretary from Professor S. W. Stratton, director of the National Bureau of Standards, Washington, D. C., and Mr. G. E. Barton with reference to the cooperation of the American Chemical Society, with the said bureau "in framing the regulations governing the examination of glassware or any other matters of general interest to chemists, and pertaining to the work of the bureau."

It was voted that the Council be requested to consider the question of discharging the present Committee on Standards for Instruments of Measure, and the appointment of a new committee to cooperate with the National Bureau of Standards as requested by Professor Stratton.

A resolution was presented by Professor W. H. Seaman, of Wash-

ington, with reference to the use of the decimal system of weights and measures, by the United States Government. Upon motion of Dr. McMurtrie, the question was referred to the Council.

In consideration of the large number of papers upon the program, it was voted that purely technical papers including details, which appear upon the program, be presented as briefly as possible in abstract. The following paper was then presented and discussed:

"Review of Metallography," by Henry Fay, which was discussed by Professors Bancroft, Fay, J. W. Richards and C. B. Dudley.

The report of the treasurer was at this time called for and presented to the Society; on motion, it was accepted and ordered placed on file.

After the treasurer's report, papers were presented and discussed as follows:

"Naturally Occurring Telluride of Gold," by Victor Lenher. Presented by Edgar F. Smith.

"Action of Selenic Acid on Gold," by Victor Lenher. Presented by Edgar F. Smith.

"The Quantitative Blowpipe Assay of Telluride Gold Ores," by Joseph W. Richards.

"A New Blowpipe Reaction for Germanium," by Joseph W. Richards.

"Potassium Perselenate," by L. M. Dennis.

"Contributions to the Chemistry of the Rare Earths of the Yttrium Group," by L. M. Dennis and Benton Dales.

"Preliminary Note on a New Separation of Thorium," by F. J. Metzger. Presented by Alfred Tingle, and discussed by Professor Bogert.

"Sodium," by J. D. Darling.

"The Determination of Silica," by W. F. Hillebrand.

President Clarke then announced the appointment of E. F. Smith, C. B. Dudley and C. E. Munroe, as a committee from the American Chemical Society to confer with those who are interested in the formation of an Electro-Chemical Society.

After some announcements, the morning session was adjourned.

The evening session of the Society was held at the Acorn Club, 1618 Walnut Street. The meeting was called to order at 8.15 P.M. Dr. J. Merritt Matthews, vice-president of the Society,

and chairman of the Philadelphia Section, was called to the chair. The address of the retiring president, Professor F. W. Clarke, was delivered upon the subject "The Development of Chemistry." After the address, the session was adjourned and the chemists attended a reception, given by the Ladies' Reception Committee in the club rooms. After the reception, a "smoker" was given at the University Club, 1510 Walnut Street.

TUESDAY, DECEMBER 31, 1901.

The Society was called to order at 9.45 A.M. The report of the election of president and councilors was presented by the secretary as follows:

*For President*—Ira Remsen, Baltimore, Md.

*For Councilors at Large*, to serve until January 1, 1905—Ira Remsen, Baltimore, Md.; Arthur A. Noyes, Boston, Mass.; T. M. Drown, Bethlehem, Pa.; C. F. McKenna, New York City.

President Clarke then introduced Professor Ira Remsen, president-elect, who spoke a few words in appreciation of the honor bestowed upon him, thanking the members of the Society for their confidence, and assuring them of his hearty desire to cooperate with them in advancing the interests of the Society.

Papers were then read and discussed as follows:

"Electro-Chemical Industries at Niagara Falls with Exhibition of Sample Products," by C. F. Chandler.

"Instantaneous Chemical Reaction and the Theory of Electrolytic Dissociation (with Experiments)," by Louis Kahlenberg, which was discussed by A. A. Noyes and Louis Kahlenberg.

"What Are the Requirements of a Course to Train Men for Work in Industrial Chemistry?" by W. A. Noyes.

"The Volumetric Estimation of Alumina and Free and Combined Sulphuric Acid in Alums," by Alfred H. White.

"Aqua Ammonia: Its Impurities and Methods of Analysis," by J. D. Pennock and D. A. Morton.

"A Method of Analyzing Oil Varnishes," by Parker C. McIlhiney.

"The Oxygen Bases: A Review," by James Lewis Howe.

"Electrolytic Deposition of Lead from Phosphoric Acid Solution," by A. F. Linn. Presented by Edgar F. Smith.

"Some Pyridine Derivatives," by J. Arthur Hayes. Presented by Edgar F. Smith.

"Latest Types of Formaldehyde Regenerators" (with demonstrations), by William Dreyfus.

The time for adjournment having arrived, the remaining papers of the program were read by title.

Upon motion of Dr. Wiley, the thanks of the Society were unanimously voted as follows :

To the Philadelphia Section of the American Chemical Society, to the Local Committee of Arrangements, to the University of Pennsylvania, to the mayor of Philadelphia and the city authorities, to Miss Fanny R. M. Hitchcock and the ladies of the Reception Committee for the delightful reception at the Acorn Club, to Dr. Owen Louis Shinn, Dr. John Marshall, and their associates for the entertainment at the University Club, and to the proprietors of the various industrial establishments, who invited the chemists to visit and inspect their works.

After some announcements by the Local Committee and the secretary, the twenty-fifth general meeting of the Society was adjourned.

During the afternoons of Monday and Tuesday, visits and excursions were made under guidance of members of the Local Committee as follows :

Baldwin Locomotive Works ; United States Mint ; City Filtration Experiment Station ; Bergner and Engel's Brewery ; Midvale Steel Co.'s works ; Barrett Manufacturing Co., working up of coal-tar oils ; United States Arsenal, special laboratory equipment ; John B. Stetson Co., manufacture of hats ; Dungan and Hood, glazed kid and morocco works ; C. H. Masland & Sons, carpet mills ; Cramps' Shipyard ; Harrison Bros. & Co., Incorporated, manufacture of chemicals and paints, electrolytic method for production of sodium ; Philadelphia Navy Yard ; United Gas Improvement Co.'s works, Point Breeze ; Gillinder & Sons, glass works ; Quaker City Dye Works ; Wetherill & Bro., white lead ; J. Eavenson & Son, soap works ; Girard College.

#### ANNUAL REPORT OF THE SECRETARY OF THE AMERICAN CHEMICAL SOCIETY FOR THE YEAR 1901.

The year 1901 has been an important one in the annals of the American Chemical Society. The twenty-fifth anniversary of the founding of the Society has been appropriately celebrated, and the occasion was signaled by the election to honorary member-

ship of the following named eminent chemists : Henry E. Roscoe and Wm. Ramsay, London, England ; Adolph von Baeyer, Munich, Germany ; Emil Fischer, Berlin, Germany ; and Georg Lunge, Zurich, Switzerland ; there has been a net increase of 218 names in the roll of membership ; the expenses of the Society have been kept so far within its income that the Finance Committee recommends the setting aside of \$1,000 as an addition to the permanent invested funds ; a very successful meeting has been held in the metropolis of the Rocky Mountain region, and an application has been made for the establishment of a local section on the Pacific Coast. The affairs of the Society have been run smoothly and prosperously and its growth has been steady and vigorous.

At the general meeting in Denver, Professor Edward Hart, who has been editor of the publications of the Society since April, 1893, announced to the members of the Council who were present that he would be obliged to resign his position as editor, and soon afterward his resignation was placed in the hands of the secretary to take effect at the close of the calendar year. Dr. Hart's accumulated duties and responsibilities in other directions engross so much of his time and attention that he was unwilling to continue to occupy an office so important to the best interests of the Society when he could not devote to it the time and energy which its duties demand. The Society is thus called upon to lose one of its most faithful and successful workers, one who has contributed largely to bring it into the front rank of the scientific bodies of the world, and who has seen its journal in his own hands attain so great an eminence as that which it now occupies. Great wisdom will be needed in the selection of his successor, but whoever he may be, we are persuaded that Dr. Hart will be glad to render him any aid in his power to enable him to gain an early knowledge and good command of the situation he must fill.

A new contract has been signed for the printing of the Journal by the Chemical Publishing Company of Easton, Pa., with terms that seem more satisfactory to both contracting parties.

An index to the first twenty volumes of the Journal has been carefully prepared and will probably be printed during the coming year. The Society has also arranged for a special memorial volume of the twenty-fifth anniversary.

The winter meeting of 1900, which was held in Chicago, and the meeting held in Denver, during the summer, were well at-

tended and very successful, and did much to awaken an interest in the Society in those sections of the country.

Just eleven years ago to-day the Society held its second general meeting at the University of Pennsylvania, where we are now assembled, and we shall find it a matter of special interest to compare the conditions then existing with those under which we now meet. By December 30, 1890, the Society had begun the career of rapid growth, prosperity and influence which it has maintained unabated since that time. It had only just commenced its upward course, however, and the year 1889 marked perhaps the lowest point which it has ever reached, not only in membership, but in its general influence. In 1889 the membership was 204, but there were forces already at work both within the Society and without which were a prophecy of the great results that were to follow. The plan of organization and administration was reconstructed and the first general meeting was held in Newport in the summer of 1890. This was followed by the second general meeting in Philadelphia, December 30th and 31st of the same year. Professor George F. Barker, of the University of Pennsylvania, had just been elected president of the Society, and the inaugural address which he delivered here eleven years ago upon "The Borderland between Chemistry and Physics" will long be remembered by those who had the privilege of listening to it. In 1890 the roll of membership of the Society was 238; to-day it is 1933. There was no local section then organized although a movement had begun which resulted in the establishment of the first local section in Rhode Island the following year; now there are 13 local sections besides that on the Pacific coast, just in process of organization. In 1890 the finances of the Society were at a low ebb, and its Journal was rather insignificant in comparison with what it is at the present time. Many of the leading chemists of the country saw no reason for being identified with the Society at all, and its influence abroad was but little. To-day the American Chemical Society may be regarded as a truly representative organization of the chemists of America, commanding their interest and support, and one of the prominent national chemical societies of the world.

Those who have been identified with its progress during the past twelve years may justly feel gratified at the results of the efforts which they have made for its prosperity. Here in Phila-

delphia an energetic local section has been recently formed, which has already attained a high rank as a local branch of the general Society.

The membership statistics for the past year are as follows :

Membership reported at Chicago meeting ....	1715
New members since qualified .....	344
Died .....	11
Dropped for arrears .....	58
Resigned .....	57
Total loss.....	126
Net gain.....	218
<hr/>	
Membership, December 26, 1901 ...	1933
Elected not qualified.....	69
Applications pending.....	73
Grand total.....	2075

Membership by classes :

Members .....	1794
Associates .....	124
Honorary members .....	15
Total.....	1933

Membership of local sections, as stated in the annual reports of the sections, October 15, 1901 :

Rhode Island Section .....	34
New York Section .....	441
Cincinnati Section .....	57
Washington Section.....	123
Lehigh Valley Section .....	17
Chicago Section .....	81
Nebraska Section .....	16
Columbus Section.....	30
North Carolina Section.....	24
North Eastern Section .....	257
Philadelphia Section.....	115
Michigan Section .....	60
Kansas City Section.....	26

Total number of members in local sections 1281

Per cent. of membership in local sections..... 66½

The following deaths have been reported since the Chicago meeting : Hermann A. Loos, of New York City ; C. Chauncey Parsons, of Brooklyn ; Lawrence S. Williams, of Chicago ; Edward L. Smith, of Worcester, Mass. ; F. O. Matthiessen, of

New York City ; Stratford Burtt, of Brooklyn ; John A. Myers, of New York City ; W. J. Youmans, of New York City ; Charles Rice, of New York City ; Philip S. Baker, of Greencastle, Ind. ; Wm. Van Slooten, of Brooklyn.

Respectfully submitted,

ALBERT C. HALE, *Secretary.*

REPORT OF THE TREASURER FROM DECEMBER 21, 1900, TO  
DECEMBER 21, 1901.

RECEIPTS.

Balance on hand, December 21, 1900.....	\$	444	31
Received for dues.....	\$8750	00	
"    "    back numbers.....	625	36	
"    "    subscriptions.....	865	16	
"    "    advertising.....	1232	46	
"    "    Michigan Section returned.....	27	86	
"    "    Cincinnati "    ".....	1	27	
"    "    life membership, Morris Loeb.....	100	00	
"    "    "    "    H. J. Davis.....	100	00	
"    "    "    "    Elihu Thompson.....	100	00	
"    "    interest on deposits.....	112	35	
"    "    "    on special investment fund.....	70	00	
"    "    "    on life membership fund.....	35	00	
			\$12,019 46
			\$12,463 77

DISBURSEMENTS.

For printing Journal.....	\$3849	38
"    authors' reprints.....	325	18
"    expense, president's office.....	100	00
"    "    editor's ".....	79	55
"    "    secretary's "    (clerical).....	618	39
"    "    "    "    (current).....	103	96
"    "    "    "    (general).....	389	64
"    "    "    "    (collection of dues).....	875	00
"    "    librarian's office.....	152	50
"    "    library (binding and completing files, 1900-1901).....	552	28
"    "    library (clerical help, 1900-1901).....	165	00
"    "    "    card catalogue.....	50	00
"    "    advertising.....	14	52
"    "    rebate on subscriptions.....	27	10
"    "    back numbers, storage, etc.....	149	60
"    "    printing directories.....	211	35
"    "    Review of American Chemical Research....	56	60
"    "    Committee on Patent and Related Legislation.....	6	86



For expense, special appropriations.....	136 57
“ “ membership committee.....	3 48
“ “ editor's salary, 1901.....	250 00
“ “ treasurer's office, 1901.....	400 00
“ “ Chicago meeting.....	93 88
“ “ Denver meeting.....	193 12
“ “ Philadelphia meeting.....	11 00
“ “ incidentals.....	120 92
	<hr/>
	\$8935 88
“ “ local sections, viz.:	
Cincinnati.....	\$ 58 33
Columbus.....	23 33
Kansas City.....	17 85
Michigan.....	58 33
Nebraska.....	26 67
New York.....	600 00
North Carolina.....	30 00
North Eastern.....	388 33
Philadelphia.....	56 65
Rhode Island.....	35 00
Washington, 1900-1901.....	218 69
	<hr/>
	\$ 1513 18
	<hr/>
	\$10,449 06
Paid H. Huntington for set of <i>Berichte</i> by life membership.....	100 00
	<hr/>
	\$10,349 06
Unpaid bills.....	312 60
	<hr/>
	\$10,036 46
Deposited in Emigrants' Savings Bank.....	470 00
	<hr/>
	\$10,506 46
Balance on hand.....	1957 31
	<hr/>
	\$12,463 77

## ASSETS.

Special investment fund (2000, 3½ per cent. N. Y. gold bond due 1915).....	\$2097 50
Life membership fund (1000, 3½ per cent. N. Y. gold bond due 1925).....	\$1080 38
In Emigrants' Savings Bank.....	319 62
“ “ “ “ from Morris Loeb..	100 00
“ “ “ “ “ H. J. Davis....	100 00
“ “ “ “ “ E. Thompson..	100 00
“ “ “ “ “ H. Huntington	100 00
Interest on bond.....	70 00
“ from bank.....	14 90
	<hr/>
	1884 90

Balance in Knickerbocker Trust Co.....	1953 08
Cash in treasurer's hands.....	4 23
" " secretary's " .....	182 25
Uncollected accounts advertising... ..	810 00
" " dues.....	1465 00
	<u>\$ 8,396 96</u>

## LIABILITIES.

Life membership fund.....	\$1884 90
Unexpended library appropriations (for binding and completing files).....	67 20
Unpaid bills.....	312 60
	<u>\$2264 70</u>
Balance of actual assets.....	6132 26
	<u>\$ 8,396 96</u>

A. P. HALLOCK, *Treasurer.*

Accounts and vouchers examined and found correct, e. and o. e.

CHAS. F. McKENNA,  
J. H. WAINWRIGHT,  
DURAND WOODMAN,  
*Finance Committee.*

## REPORT OF THE LIBRARIAN.

Total number of copies of the Proceedings and the Journal in stock December 20, 1901 :

In storage warehouse.....	36,209
At Chemists' Club.....	15,824
Total .....	<u>52,033</u>

Copies sent out by librarian during the year ending December 20, 1901 :

Complete volumes.....	130
Single numbers .....	2,657

There were sold during the year 96 complete volumes, and 383 single numbers.

The total amount received from sales of the Proceedings and the Journal from December 15, 1900, to December 1, 1901, and transmitted to the treasurer, was.....\$609 86

Uncollected accounts..... 19 76

The following is an account of binding and completing files of Journals in the library :

DR.

Dec. 18, 1900. To balance of appropriation for 1900 (contracted for).....	\$219 48
Jan. 1, 1901. To appropriation for 1901 .....	400 00
	<u>\$619 48</u>

(23)

CR.

By purchase of 157 volumes and 307 single numbers to complete files .....	\$270 88	
By binding 354 volumes .....	281 40	
		<u>552 28</u>
Balance December 1, 1901 (contracted for) .....		\$67 20

Account of general expenses of librarian's office for year ending December 1, 1901:

DR.

December 1, 1900. To balance .....	\$ 10 07	
To cash, A. P. Hallock, treasurer .....	152 50	
		<u>\$162 57</u>

CR.

By postage .....	\$68 19	
By stationery and printing .....	15 05	
By library supplies .....	23 81	
By express and incidentals .....	44 79	
		<u>151 84</u>
Balance .....		\$ 10 73

The appropriation of \$100 for clerical services has been expended for general clerical services and in cataloguing the library.

Donations to the library have been received from A. C. Hale, C. F. McKenna, A. P. Hallock, and Edward Hart.

There are six issues of the Journal of which we have less than twenty copies each. Of Volume XXII, No. 2, there are but ten copies remaining.

The card catalogue of the library is practically completed. It shows about 4,000 books and pamphlets as the property of the Society, and about 650 as belonging to the Chemists' Club.

The Society's library will contain, on the completion of the files represented, a good collection of the more important chemical journals, and many of those on general science. It contains, however, very few modern publications on special subjects.

The appropriations made by you in the past two years were needed, and they have been employed in completing the existing files of Journals, and in bringing the binding of the library to date. Much remains to be done in this direction, however. Many missing volumes and numbers we shall probably never obtain except as we may purchase complete sets. At present this is not advisable, unless there is some immediate prospect of

disposing of what would, under such circumstances, become duplicate material.

The Chemists' Club is endeavoring, by voluntary subscriptions, to meet the need of monograph works, and it is hoped that in time we may have in the combined libraries of the Society and the Club a good reference library. Respectfully submitted,

E. G. LOVE, *Librarian.*

### COUNCIL.

The Council was called to order by President Clarke, in Room 1, Houston Hall, at 2 P.M. The following members of the Council were in attendance: Messrs. Clarke, Munroe, Remsen, Hillebrand, Dudley, Sadtler, Talbot, A. A. Noyes, W. A. Noyes, Marshall, Long, Morley, Kinnicutt, Catlin, Wiley, McMurtrie, Hallock, Sabin, McKenna, Hale, Doremus, Evans, and Baskerville.

The minutes of the Council as printed in the Journal were approved.

An application for the formation of a local section to include the territory of the state of California, with headquarters at San Francisco, was presented by the secretary, and, upon motion, the application was granted by the Council.

The Council voted that the names of all candidates for membership presented up to the close of the twenty-fifth general meeting, are herewith passed upon favorably by the Council, and the candidates shall be notified by the secretary of their election to membership, whenever all the other requirements in their case shall be fulfilled.

It was voted that the next general meeting of the Society shall be held in Pittsburg, Penna., June 30 and July 1, 1902, in connection with the meeting of the American Association for the Advancement of Science.

The secretary presented the final report of the Committee on the Twenty-Fifth Anniversary of the Society; the report was accepted and the committee discharged with thanks.

The Committee on Title Index and also the Committee on the New Contract for Printing the Journal, having performed their duties, were, at their own request, discharged.

The resignation of H. Carrington Bolton, as chairman of the

Committee on Exchanges, was presented by the secretary and accepted by the Council.

It was voted that a file of the Journal and the Proceedings of the Society from the beginning, be kept in the office of the secretary for his official use.

It was voted that the secretary be allowed, at his discretion, to send samples of the Journal of the Society to applicants for membership.

The resignation of William McMurtrie, as chairman of the Committee on Conference with Section C of the American Association for the Advancement of Science, was accepted, and the president of the Society, *ex-officio*, was appointed chairman in his place.

The president was authorized to appoint some person to collect, arrange and transmit to the Committee on Publications all matter intended for the twenty-fifth anniversary volume.

It was voted that the secretary collect the membership dues during the year 1902, as heretofore, and that he be allowed 10 per cent. commission on all sums so collected, as compensation for his services.

The librarian was authorized to use his discretion in the matter of enforcing the rule requiring complaints for non-receipt of the Journal to be made within sixty days from the first day of the month corresponding to the missing number of the Journal.

It was voted that the Council favors the publication of addresses and advance notices regarding the Society and its sections in the periodical "*Science*."

The resignation of Dr. Edward Hart, as editor of the Journal, was accepted, and the thanks of the Council were voted unanimously to Dr. Hart for the able manner in which he has conducted the Journal.

It was voted that nominations be received for the office of editor; the following persons were then nominated: Edgar F. Smith, nominated by C. B. Dudley; W. A. Noyes, nominated by A. A. Noyes. The nominations were then closed, and Drs. Hallock and Long were appointed tellers to prepare, distribute and collect the ballots. Upon the first ballot the tellers reported a tie vote, Drs. Smith and Noyes each having received 11 ballots. Upon the second ballot for editor, Dr. Noyes received 13 votes

and Dr. Smith, 9; Dr. Noyes was therefore declared elected editor for the year 1902.

The president having ruled that it was competent for the Council to elect the remaining officers, eligible by that body, instead of merely placing them in nomination, the following named persons were elected to fill the respective offices mentioned:

*Secretary*—Albert C. Hale.

*Treasurer*—Albert P. Hallock.

*Councilor* (to serve in place of Ira Remsen, elected president)—Ernest E. Smith.

*Councilor* (to serve in the place of W. A. Noyes, elected editor)—Edward Hart.

*Directors* (to serve till January 1, 1904)—E. E. Smith, C. F. Chandler.

*Committee on Papers and Publications*—W. A. Noyes, Editor, Chairman; W. F. Hillebrand, J. H. Long, William McMurtrie, Arthur A. Noyes, Edward Hart, Edgar F. Smith, H. N. Stokes, H. P. Talbot, H. W. Wiley.

*Finance Committee*—J. H. Wainwright, Durand Woodman, C. F. McKenna.

*Committee on Membership*—William McMurtrie, C. L. Reese, E. G. Love.

The following was adopted as the budget of expenditures for the year 1902:

Journal and abstracts.....	\$4,500
Authors' reprints.....	350
Index, Volumes I to XX, inclusive.....	300
Twenty-Fifth Anniversary volume.....	500
Editor's salary.....	500
Editorial expenses:	
Abstract editor's salary.....	150
Abstract fees.....	300
Expenses of editor and abstract editor.....	200
Collection of dues, 10 per cent. of dues received.....	1,000
General meetings.....	300
Directories.....	250
Local sections.....	1,500
Office of secretary.....	1,300
Office of treasurer.....	400
Office of librarian.....	1,000
Committees.....	75
Special appropriations.....	750
Total.....	\$13,375

It was moved by W. A. Noyes, that the edition of the Journal for the first three months of 1902 be made 3,000 copies, and, after that, 2,800 copies; the motion was duly seconded and carried.

It was voted that the chairman of the Committee on Advertising be authorized to make such arrangements for soliciting advertising and management of the business connected therewith, as in his discretion seems best for the interests of the Society.

It was voted that the librarian be chairman of the Committee on Exchanges, and that the president be made a member *ex-officio*, in place of Dr. H. C. Bolton, resigned.

It was voted that the balance of funds in the hands of the Twenty-Fifth Anniversary Committee, after defraying all expenses of such committee, be turned into the treasury of the Society.

It was voted that the Council recommends to the Directors that President F. W. Clarke be reimbursed for the expenses of his office during the year 1901 in excess of the appropriation made for that purpose in the annual budget of the Society for said year.

Mr. E. E. Ewell, chairman of the Committee on Standards for Instruments of Measure, presented a communication which was received, and, at the request of the chairman, the committee was discharged with the thanks of the Council.

The secretary presented the following communication which had been received by President Clarke :

TREASURY DEPARTMENT, NATIONAL BUREAU OF STANDARDS,  
WASHINGTON, December 12, 1901.

PROF. F. W. CLARKE, *President American Chemical Society,*  
*Washington, D. C.*

DEAR SIR :—I have the honor to inform you that the National Bureau of Standards is preparing to take up the work of testing chemical glassware. We would be pleased to cooperate with the Society of which you are president in framing the regulations governing the examination of glassware, or any other matters of general interest to chemists and pertaining to the work of the Bureau.

Respectfully,  
S. W. STRATTON,  
*Director.*

The president was authorized to appoint a committee for co-

## ASSOCIATES ELECTED JANUARY 11, 1902.

Blair, Frank W., 95 Newbury St., Boston, Mass.  
 Carleton, Spencer, 62 W. 49th St., N. Y. City.  
 Esquerré, Edmond, 116 W. 114th St., N. Y. City.  
 Hershey, Elam, Buffalo Union Furnace Co., Buffalo, N. Y.  
 Lang, G. Bryant, 844 N. 20th St., Philadelphia, Pa.  
 Mack, Joseph L., 1127 S. 48th St., Philadelphia, Pa.  
 Miller, Howard E., Rose Poly. Inst., Terre Haute, Ind.  
 Odell, J. R., 157 Huntington Ave., Boston, Mass.  
 Richardson, William D., Box 185, Fredericksburg, Va.  
 VanAldridge, Earl, 1122 Washtenaw Ave., Ann Arbor, Mich.  
 Williams, R. S., 189 St. Botolph St., Boston, Mass.

## NAMES PROPOSED FOR ASSOCIATE MEMBERSHIP.

Plank, W. F., State College, Pa.  
 Wiedemann, H. Edmund, 944 N. 8th St., Terre Haute, Ind.

## CHANGES OF ADDRESS.

Ackerman, Franz W., 86 Pierrepont St., Brooklyn, N. Y.  
 Arnott, Geo. W. Campbell, 12 Richmond St., E., Toronto, Canada.  
 Atwood, F. W., 216 Milk St., Boston, Mass.  
 Bosart, L. W., Jr., Bond Hill, Ohio.  
 Browning, Chas., Jr., 2107 22nd St., Sacramento, Cal.  
 Buck, C. Austin, 521 Locust St., So. Bethlehem, Pa.  
 Byrnes, Eugene, 918 F. St., Washington, D. C.  
 Cady, W. B., Ypsilanti, Mich.  
 Campbell, E. D., 1555 Washtenaw Ave., Ann Arbor, Mich.  
 Carveth, Hector R., 115 Cook St., Ithaca, N. Y.  
 Corse, W. M., 14 Piquette Ave., Detroit, Mich.  
 Dales, Benton, 115 Cook St., Ithaca, N. Y.  
 Dean, W. H., 167 W. River St., Wilkes-Barre, Pa.  
 Desper, Ernest W., 16 Kendall St., Worcester, Mass.  
 Earle, Richard B., 15 Hollis Hall, Cambridge, Mass.  
 Edgar, C. G., 87 Watson St., Detroit, Mich.  
 Fasset, Chas. M., 702 Main Ave., Spokane, Wash.  
 Fowler, Roy E., 502 University Ave., Ithaca, N. Y.  
 Green, Erik H., 14 John St., Providence, R. I.  
 Griffith, S. H., 3108 New Hampshire Ave., Washington, D. C.  
 Guess, H. A., Silver Lake Mines, Silverton, Colo.  
 Hancock, W. J., 147 Remsen St., Brooklyn, N. Y.  
 Harris, I. F., Box 43, New Haven, Conn.  
 Harsh, S. A., Box 910, Denver, Colo.  
 Hartzell, Harry S., 126 N. 4th St., Allentown, Pa.  
 Heckel, Fred. J., Box 1201, Butte, Montana.  
 Hildreth, Thomas F., Pittsburg Steel Foundry, Glassport, Pa.  
 Koch, F. C., 208 W. Elm St., Urbana, Ill.  
 Krebs, August S., Care of Krebs Pigment & Chem. Co., Newport, Del.



Lamar, Wm. R., care Mallinckrodt Chem. Works, St. Louis, Mo.

Lanning, John G., 106 Miles Ave., Cleveland, Ohio

Leffmann, Henry, 119 So. 4th St., Central Sta., Philadelphia, Pa.

Mahon, R. W., N. Y. C. and H. R. R. West Albany, N. Y.

Mathewson, E. P., care J. A. Mathewson & Co., Montreal, Canada.

Matthews, J. Merritt, 225 S. 45th St., Philadelphia, Pa.

McLoughlin, Charles, 890 Broadway, N. Y. City.

Merzbacher, Aaron, Lab. Reading Iron Co., Reading, Pa.

Moale, Philip R., Secy.-Treas. Asheville Ptg. Co., Asheville, N. C.

Moody, Herbert R., 616 Main St., Geneva, N. Y.

Pennington, Miss Mary E., 3914 Walnut St., Philadelphia, Pa.

Perkins, G. E., 5 Adie St., Providence, R. I.

Perkins, T. S., 318 California St., San Francisco, Cal.

Peter, Alfred M., Chemist Ky. Agr. Expt. Sta., Lexington, Ky.

Phalen, Wm. C., 305 Broadway, Cambridge, Mass.

Pitman, John, National Armory, Springfield, Mass.

Quinan, K. B., Care of De Beers Explosives Works, Somerset West, Cape Colony, S. Africa.

Rademacher, H. A., Law Office of Pierson & Pease, Chamber of Commerce, Chicago, Ill.

Rand, Charles L., 105 Quarry St., Ithaca, N. Y.

Rauchfuss, Eugene J., 36th St. and 1st Ave., N. Y. City.

Remington, J. Percy, 417 Bourse, Philadelphia, Pa.

Richardson, W. D., care Swift & Co., National Stock Yards, E. St. Louis, Ill.

Riddell, Dell F., Sioux Falls Coll., Sioux Falls, S. D.

Ripley, Philip F., Assabet Mills, Maynard, Mass.

Sadtler, S. S., N. E. Corner 10th and Chestnut Sts., Philadelphia, Pa.

Sparks, John C., The De La Vergne Refrig. Co., Foot of E. 138th St., N. Y. City.

Tobin, J. J., 35 Pelham St., Newport, R. I.

Van der Linde, Harold T. G., 47-50 Front St., W., Toronto, Canada.

Voorhees, L. A., Box 357, New Brunswick, N. J.

## BOARD OF DIRECTORS.

The meeting was called to order by President Clarke, immediately after the adjournment of the Council. The following named Directors were present : Clarke, Hale, Hallock, and Doremus.

It was voted that all action and recommendations of the Council pertaining to matters of finance or to the business of the Soci-

ety, which come legitimately before the Directors, are hereby approved and adopted by the Directors.

A communication from the Chemical Publishing Company requesting certain back numbers of the Journal to be used in connection with the printing of the Journal, was presented by the secretary, and it was voted that said numbers be transmitted to the Chemical Publishing Company, in trust, for use in the interests of the Society.

It was voted that a copy of the current numbers of the Journal be furnished the treasurer of the Society, in trust, for use in his office.

The communication from the Finance Committee with reference to the investment of \$1,000 of the funds of the Society, was presented by the secretary, but on account of the amount which had been adopted in the budget of the Society for the year 1902, it was deemed unwise, at present, to draw any funds from the treasury for investment.

The meeting of the Directors was then adjourned.

ALBERT C. HALE, *Secretary*.

## MEETINGS OF THE SECTIONS.

### WASHINGTON SECTION.

The one hundred and twenty-ninth regular meeting was held November 14. The following program was presented :

"The British Municipal Laboratories," by H. W. Wiley ;  
 "Alfred Nobel and the Nobel Prizes," by C. E. Munroe ; "Experience with Several Methods used in Detecting Process Butter," by G. E. Patrick.

The last paper treated at length of the Hess and Doolittle method, microscopic examination, and the Waterhouse test ; briefly of the boiling test.

Under the Hess and Doolittle method, the examination of the dried curd with a low-power microscope was tried upon 53 samples of known character. Considerable difficulty was experienced in interpreting the appearances presented in some instances, but in the majority of cases the appearances were decisive. A modification is suggested which it is hoped will render the results more uniformly decisive. "While there is room for much improvement in this test, even as it stands it is to be classed among the useful corroborative tests available to the chemist."

The other and principal part of the Hess and Doolittle method has to do with the soluble and insoluble proteids of the curd and brine. The paper shows that the ratio claimed by Hess and Doolittle

little to exist between the soluble and insoluble proteids of process butter is not to be relied upon as a means of distinguishing between this kind of butter and the genuine. The reason for this is shown to lie in the fact that the soluble proteid in fresh process butter is mainly casein, and as the butter ages this casein coagulates, and thus in time the soluble protein may be reduced to an amount as small as that of genuine butter, perhaps smaller.

Under the microscopic examination of butter the paper states that some process butters are now so well made, that is, the melted fat is so rapidly cooled, that it is in some instances practically free from traces of crystallization, so that they are as free from crystalline, flaky, or frosty appearance, when viewed with polarized light and crossed nicols, as are a great many genuine butters that have been ill treated as to temperature. The paper emphasizes the importance of observing the size and abundance of the casein particles in butters, since process butters, as a rule, contain many more large casein spots than do well made genuine butters. Some "country butters," however, approach or equal process butters in this regard; creamery butters seldom, if ever, do.

The paper describes a mode of using the Waterhouse test, with water as the medium instead of milk, and under certain temperature conditions, for the purpose of determining whether a butter is "surely genuine" or not; that is, whether or not it is above suspicion of being a process butter.

---

The one hundred and thirtieth regular meeting was held December 12. The following program was presented:

"The Solubility of Mixtures of Sodium Chloride and Sodium Sulphate," by A. Seidell.

The author first gave a brief summary of the status of solubility work in solutions other than very dilute ones, and described in detail the experimental difficulties which have to be met in this kind of work. He then presented a diagram, illustrating the solubility curves for the system  $\text{NaCl}-\text{Na}_2\text{SO}_4-\text{H}_2\text{O}$  at  $10^\circ$ ,  $21.5^\circ$ ,  $25^\circ$ ,  $27^\circ$ ,  $30^\circ$ ,  $33^\circ$ , and  $35^\circ$ . It was shown that at temperatures above  $33^\circ$ , the curves represented equilibrium conditions between sodium chloride and anhydrous sodium sulphate, and no abnormalities presented themselves. Between  $33^\circ$  and  $17^\circ$ , however, it was found that in solutions containing but small amounts of sodium chloride and in contact with solid sodium sulphate, the equilibrium conditions were determined by the solid salt being in the form of the decahydrate, and the solubility curves for this decahydrate are very much flatter than the corresponding curves for the anhydrous salt. But as the amount of sodium chloride in the solution increased, at temperatures between  $33^\circ$  and  $17^\circ$ , there was always a sudden change in the direction of the solubility curve for sodium sulphate, which was found to be caused

by the sodium sulphate present as solid phase, having gone over to the anhydrous form. In order to check this view, the experiment was made of placing large well-formed crystals of sodium sulphate decahydrate in two test-tubes, one containing a saturated solution of sodium sulphate alone and the other a solution nearly saturated with sodium chloride, as well as sodium sulphate. Both test-tubes were fitted with cork stoppers carrying thermometers. They were then immersed in a water-bath and the temperature gradually raised. At  $28^{\circ}$  the crystals in the sodium chloride solution gradually became opalescent around the edges, then rather rapidly became entirely opaque and showed a tendency to fall apart in a loose powder. The material had undoubtedly gone over to the anhydrous salt, although the crystals which were in the tube containing only water and sodium sulphate showed no change until the temperature reached  $33^{\circ}$ . It thus appeared that the transition temperature for the change of sodium sulphate decahydrate to anhydrous salt had been displaced by the presence of sodium chloride. This was regarded as of considerable significance, and is important in connection with the suggestions on this subject in the study of the change of gypsum to calcium sulphate hemihydrate, made by Van't Hoff and Armstrong, Vater, and Cameron.

The solubility curves for sodium sulphate heptahydrate in solutions of sodium chloride were shown to be very similar to those for the decahydrate. In the case of the decahydrate at lower temperatures and the heptahydrate, the curves were shown to have minimum points, the significance of which is not apparent at the present time.

"The Evolution of Metallic Retorts" (with samples). By W. H. Seaman.

Before commencing the paper, the speaker showed a very perfect copy, just received from England, of Boerhaave's "New Method of Chemistry," in two volumes, second edition, 1741. Boerhaave was born in 1668, died in 1738, was famous as a physician, botanist, and chemist, and was one of the first to recognize the independence of the latter science.

The first metallic retorts were copper flasks just like the olive oil flasks of the early chemists with a gallows screw added. In a lot of scrap of Prof. Henry's apparatus about to be sold thirty years ago, the author found two wrought-iron retorts, with walls a centimeter thick, and shaped just like a glass tubular retort, that are types of this class.

The next retort exhibited was a pear-shaped vessel. It had a feed-wheel on top, and was set in an egg stove, the bottom made red hot, and potassium chlorate fed in by the wheel. The oxygen was taken off by the side pipe.

Next was a kettle-shaped retort patented by the author. Its

peculiarity is that all parts are drawn together by the gallows screw, while the top is durable with ground joint, and the bottom being thin, heats quickly and can be cheaply renewed.

Next we have the cylindrical sheet-metal retort which admits of moving the Bunsen burner along its length so as to decompose the charge in successive portions.

The latest development is the little frustrum of a cone, with gallows screw top and two pipes, one for delivery and one for the introduction of an inert gas, or other purposes that may be desired. In this, oxygen may be made, coal distilled, etc. They are sold by the Chicago Laboratory Supply Co., price, \$1, and are one of the most useful acquisitions lately made to laboratory apparatus.

"Starch as an Adulterant or Drier in Butter, and a Study of Glucose in Butters." By G. E. Patrick and D. Stuart :

(1) The paper describes first a canned butter which was found to contain, besides about 15 per cent. of glucose, 3.15 per cent. of starch, either potato starch or a variety closely resembling it. The starch was probably added as a drier; it is said to be sometimes used for this purpose in remanufactured butter. The complete analysis of this butter was: water, 27.19; fat, 40.36; ash, 12.65 (all NaCl except 0.65 impurities); casein ( $N \times 6.25$ ), 0.86; starch, 3.15; other organic matter, 15.8 per cent. Assuming 0.3 per cent. of lactose, there remains 15.5 per cent. of organic matter which was set down as glucose, since no other organic substance was identified. The aqueous extract, of 100 cc. volume, from 26.05 grams of the butter, that is, a "normal sugar solution," polarized 26.2 degrees on the cane-sugar scale (Soleil-Ventzke).

(2) With four glucosed butters studied, whose "normal sugar solutions" polarized, respectively,  $7.0^\circ$ ,  $11.0^\circ$ ,  $18.5^\circ$ , and  $26.2^\circ$ , and whose percentages of organic matter designated glucose (as in the case above) were respectively, 7.0, 7.9, 10.6 and 15.5 per cent., the rotary and copper-reducing powers of the aqueous extracts being referred to these amounts of dry matter; the copper-reducing power was in every case (possibly, excepting one) too low to correspond to the rotary power, according to Rolfe and Defren, if the entire matter were pure glucose. Sucrose was suspected, and inversion was tried by means of saccharin, following the method of Tolman. In only two of the four cases was the rotation appreciably lowered. In these two, and these two butters were canned by the same firm, there was a marked reduction of rotation, indicating (of course, not proving) the presence of cane-sugar to the amount of about 1.3 per cent. on the butters. The increase of copper reduction, by inversion, was not determined at the time, but several weeks later, the small residual samples having been meantime at laboratory temperature, one was tested and the increased copper reduction, after inversion, was found to

correspond to 0.83 per cent. sucrose in the butter, while the decrease of rotation by inversion at this time corresponded to only 1.0 per cent. sucrose. As glucose is added to butters in the form of a sirup, and as there are upon the market glucose sirups containing admixture of cane-sugar, the presence of the latter in a glucosed butter need not be so very surprising. Aqueous extracts, "normal sugar solutions" of 49 non-glucosed butters, polarized from  $0.0^{\circ}$  to  $0.5^{\circ}$ , averaging  $0.22^{\circ}$ . Five ladled butters out of 15 examined, polarized from  $3.4^{\circ}$  to  $5.7^{\circ}$ , showing admixture of glucose. Glucose is frequently used by ladlers to improve the appearance of their product.

L. S. MUNSON, *Secretary*.

#### COLUMBUS SECTION.

Since the Summer vacation the Columbus Section of the American Chemical Society has held three regular meetings. At the first of these, the following officers were elected for the year:

*President*, H. A. Weber.

*Secretary*, W. E. Henderson.

*Treasurer*, E. T. Watson.

*Councilor*, William McPherson.

*Committee on Membership*.—C. C. Howard, G. B. Kauffman, A. M. Bleile.

At this meeting, quite a number of associate members was elected, and a number of names have been added to the list of active members so that the Section is in a prosperous condition.

The meeting for November was devoted to a detailed description of the chemical work in progress at the present time in Ostwald's laboratory at Leipzig, the paper of the evening being read by Professor C. W. Foulk, of the Ohio State University.

The program for the December meeting consisted of a full report of the Denver meeting of the American Association for the Advancement of Science, Professor McPherson reporting upon the meetings and papers, and Professor Weber upon the excursions.

W. E. HENDERSON, *Secretary*.

## Proceedings.

### COUNCIL.

The following motion was made by William McMurtrie, and has been approved by the Council :

"Be it resolved : That the thanks of the American Chemical Society, through its Council, be and are hereby expressed to Mrs. M. W. Dittmar, of 120 W. 130th St., New York, N. Y., for valuable contribution to the Library of the Society of ninety-nine volumes of works on chemistry."

#### NAMES PROPOSED FOR MEMBERSHIP.

Aldrich, Charles H., Perth Amboy, N. J.  
Adler, Leon L., 100 William St., N. Y. City.  
Arey, Albert L., 1148 Pacific St., Brooklyn, N. Y.  
Ash, Charles S., 141 Fell St., San Francisco, Cal.  
Barber, René R., Georgetown, Ontario, Can.  
Bauer, G. W., 1722 Buchanan St., San Francisco, Cal.  
Bird, R. M., Agricultural College, Miss.  
Carter, John P., 626 S. 24th St., Philadelphia, Pa.  
Cohn, Alfred I., 14 E. 97th St., New York City.  
Eckart, Charles F., Honolulu, H. I.  
Ellis, Wm. H., School of Practical Science, Toronto, Canada.  
Harrell, George R., Copperfield, Vt.  
Haynes, Herman W., 3 Dudley Pl., Worcester, Mass.  
Kennedy, Mortimer B., 523 Madison St., Ann Arbor, Mich.  
Kinney, Charles N., Drake Univ., Des Moines, Iowa.  
Klein, Arthur, Box 678, Erie, Pa.  
Kramer, Stephen S., care Chas. Pfizer & Co., 11 Bartlett St., Brooklyn, N. Y.  
Lang, Wm. R., Univ. of Toronto, Toronto, Canada.  
Lawson, William, Alameda Sugar Co., Alvarado, Cal.  
Lee, Theophilus H., care of Mr. F. D. Aller, Antofagasta, Chili.  
Mathews, Albert P., Univ. of Chicago, Chicago, Ill.  
McQueen, H. J., El Dorado Oil Works, West Berkeley, Cal.  
Morse, Willard S., Apartado A, Aguascalientes, Mexico.  
Oliver, Roland L., 101 Vernon St., Oakland, Cal.

Perley, William M., 1846 E. Belmont Ave., Chicago, Ill.  
Randall, Charles W., High School, Lockport, N. Y.  
Robinson, Franklin C., Bowdoin College, Brunswick, Me.  
Sampson, (Miss) Ethel V., 957 Washington St., Newtonville,  
Mass.  
Searby, F. W., El Dorado Oil Works, West Berkeley, Cal.  
Shoemaker, Harry I., 4205 Mason Ave., Tacoma, Wash.  
Smith, Francis P., 124 Sansome St., San Francisco, Cal.  
Snow, Frank J., Chem. Lab., Internal Revenue Office, Ap-  
praisers' Building, San Francisco, Cal.  
Taylor, M. A., 25 East St., New Castle, Pa.  
Tompkins, Philip W., 123 California St., San Francisco, Cal.  
Werner, David T., 114 South 9th St., Lebanon, Pa.

NAME PROPOSED FOR ASSOCIATE MEMBERSHIP.

Collins, Ward C., 3424 Wabash Ave., Chicago, Ill.  
Simmons, John P., 46 Park Ave., Yonkers, N. Y.

NEW MEMBERS ELECTED FEBRUARY 8, 1902.

Abbott, Francis L., Eveleth, Minn.  
Andrews, Clement W., The John Crerar Library, Chicago.  
Ashbrook, Donald S., 3614 Baring St., Philadelphia.  
Breazele, J. F., Bureau of Soils, Dept. of Agr., Washington,  
D. C.  
Brown, Bailey E., Bureau of Soils, Dept. of Agr., Washington,  
D. C.  
Burd, John S., Bureau of Chemistry, Dept. of Agr., Washington,  
D. C.  
Cox, Alvin J., Stanford University, Cal.  
Dunlap, Eugene E., 2016 N. 11th St., Philadelphia, Pa.  
Easton, Wm. H., 224 S. 43rd St., Philadelphia, Pa.  
Emery, William O., Crawfordsville, Ind.  
Eyles, Arthur H., Addingham, Pa.  
Fernberger, Harry M., 43 Central Ave., Waterbury, Conn.  
Fulweiler, Walter H., 4121 Girard Ave., Philadelphia, Pa.  
Graham, J. Howard, 2108 N. Marshall St., Philadelphia, Pa.  
Haas, Harry L., 526-530 W. 25th St., N. Y. City.  
Hayes, Edgar B., care S. and S. Packing Co., Kansas City,  
Kans.  
Hunter, H. B., S. E. Corner 36th St. and 1st Ave., N. Y. City.  
Kammerer, Alfred L., 391 Dormitories, Univ. of Pa., Philadel-  
phia, Pa.  
Kollock, (Miss) Lily G., 1926 Spring Garden St., Philadelphia,  
Pa.  
Masson, Victor E., Hammondsport, Steuben Co., N. Y.  
Matthews, Charles R., 3313 Prytania St., New Orleans, La.



McCoy, Herbert N., Kent Chem. Lab., Univ. of Chicago, Chicago, Ill.

Moerk, Frank X., 145 N. 10th St., Philadelphia, Pa.

Monfort, W. F., Marietta, O.

Montgomery, Thomas S., 39th and Baring Sts., Philadelphia, Pa.

Ransom, J. H., 125 S. Grant St., W. Lafayette, Ind.

Smith, Carl E., 1700 Fitzwater St., Philadelphia, Pa.

Smith, Frank R., Wilmington, Del.

Smith, Roy B., Colgate Univ., Hamilton, N. Y.

Spayd, Charles H., 48 N. 51st St., Philadelphia, Pa.

Taite, Samuel S., 4708 Windsor Ave., W. Philadelphia, Pa.

Talbot, (Miss) Marion, Univ. of Chicago, Chicago, Ill.

Thompson, Kirk W., 4 Burton Ave., Beverly, Mass.

Warfel, R. R., Allegheny S. and I. Co., Avenue, Pa.

Weston, Berne F., Monessen, Pa.

Whittlesey, Theodore, Ithaca, N. Y.

Wyman, Levi P., 1350 S. 46th St., Philadelphia, Pa.

#### ASSOCIATES ELECTED FEBRUARY 8, 1902.

Larcar, H. C., Deoghur, Baidyanath, India.

Stuart, (Miss) Emma L., 5485 Hays St., Pittsburg, Pa.

#### NEW MEMBERS ELECTED FEBRUARY 22, 1902.

Blaisdell, Albert C., N. Woburn, Mass.

Bowen, John R., Tarentum, Pa.

Clark, Friend E., Johns Hopkins Univ., Baltimore, Md.

Fischer, Richard, Madison, Wisconsin.

Folin, Otto, McLean Hospital, Waverley, Mass.

Gatchel, Joshua L., 47 Avenue C, Bayonne, N. J.

Gillman, Robert G., State Normal School, Terre Haute, Ind.

Harcourt, R., Ontario Agr. Coll., Guelph, Ontario.

Haslwanter, Charles, 904 Flushing Ave., Brooklyn, N. Y.

Hopkins, Matthew S., Royleton, cor. North and Maryland Aves., Baltimore, Md.

Kauffman, Warren L., Box 2, Yonkers, N. Y.

Lewis, Frederick H., Craigsville, Va.

Lord, E. C. E., 1910 I St., Washington, D. C.

Lowenstein, Arthur, 2538 Moorman Ave., Walnut Hills, Cincinnati, O.

Marsh, Harry B., Penn. Mil. College, Chester, Pa.

McKee, Ralph H., Lake Forest, Ill.

Newkirk, C. C., 614 W. 9th St., Cincinnati, O.

Pate, W. F., Urbana, Ill.

Seeler, Felix, care Geo. Lueders & Co., Elizabeth, N. J.

Van Arsdale, G. D., Room 68, 99 John St., N. Y. City.

Vorce, LaFayette D., 5225 Madison Ave., Chicago, Ill.  
Wahlenberg, John A., care Orford Copper Co., New Brighton,  
N. Y.

ASSOCIATE ELECTED FEBRUARY 22, 1902.

Johnston, Richard H., 972 Park Pl., Brooklyn, N. Y.

CHANGES OF ADDRESS.

Abbott, Francis L., 7714 Hawthorn Ave., Auburn Park, Chicago, Ill.

Bloomfield, L. M., Paso del Curo, Vera Cruz, Mexico.

Clevenger, G. H., care Dakota Mining & Milling Co., Deadwood, S. D.

Dewey, Elbert E., 199 Warren Ave., Chicago, Ill.

Duryea, Chester B., The Earlington, West 27th St., New York City.

Fritchle, Oliver P., care The Boston & Colorado Smelting Co., Argo, Colo.

Getz, Wm. H., 2740 Locust St., St. Louis, Mo.

Herty, Chas. H., Acilla, Ga.

Hofmann, Ottokar, care Southwest Chem. Co., Argentine, Kans.

Hopkins, Erastus, 60 William St., Worcester, Mass.

Hough, George J., 2235 Sheridan Road, Evanston, Ill.

Mackenzie, J. K., 1104 Rookery Bldg., Chicago, Ill.

McDowell, Alex. H., 457 W. 21st St., New York City.

Miller, S. C., 1220 H. St., N. W., Washington, D. C.

Moffatt, Miles R., care Mallinckrodt Chemical Co., St. Louis, Mo.

Pierson, W. C., care N. Y. Cement Co., Le Fever Falls, Ulster Co., N. Y.

Roberts, Chas. C., 339 N. Franklin St., West Chester, Pa.

Smith Horace T., care The Farist Steel Co., 137 E. Main St., Bridgeport, Conn.

Whitaker, De Berniere, Spanish-American Iron Co., Daiquiri, Santiago de Cuba.

Wiley, Samuel W., care Bowker Fertilizer Co., Elizabethport, N. J.

MEETINGS OF THE SECTIONS.

WASHINGTON SECTION.

At the meeting, which took place January 9, 1902, the following officers were elected for the present year: *President*, W. F. Hillebrand; *Vice-Presidents*, Frank K. Cameron, E. E. Ewell; *Secretary*, L. S. Munson; *Treasurer*, F. P. Dewey; *Executive*

*Committee*, W. F. Hillebrand, Frank K. Cameron, E. E. Ewell, L. S. Munson, F. P. Dewey, H. Carrington Bolton, L. M. Tolman, W. H. Seaman, V. K. Chesnut, H. N. Stokes.

L. S. MUNSON, *Secretary*.

#### KANSAS CITY SECTION.

The seventh regular meeting was held on October 8, 1901, at 714 Wyandotte Street, Professor Bailey presiding.

Prof. E. H. S. Bailey, of Kansas University, read the paper of the evening, entitled "Methods of Classification of Mineral Waters."

The author, in his work on the mineral waters of Kansas, has made a study of the methods of classification used by different authors. He admits that on account of the fact that the constituents of one water shade into those of another, the method of classification must be largely arbitrary. After mentioning the systems used by different authors down to the latest writers, he suggests that a system based on the predominant ions present may be used. In accordance with this, the arrangement would be:

I. Chloride group, or those in which the chlorine ion is the predominant one.

II. Sulphate group, in which there is a predominance of sulphates.

III. Chlor-sulphate group, or waters which contain about equal amounts of chlorine and sulphate ions.

IV. Carbonate group, or those in which carbonate ions are abundant.

V. Chlor-sulpho-carbonate group, containing considerable quantities of each of these ions.

VI. Sulphide group, or those waters which give off hydrogen sulphide, the so-called sulphur waters.

VII. Chalybeate or iron group, which includes also those containing manganese ions.

VIII. Special group, or those waters which owe their value to some special substances like lithia or borax.

IX. Soft water group, including those waters which contain only small quantities of mineral substances.

Over ninety mineral waters of the state are classified according to this system.

A motion was passed to thank Prof. Bailey and request him to give his paper to be filed with the records of the Society.

The eighth regular meeting of the section was held on November 12th, Professor Bailey presiding.

Dr. Petros F. Nishkian, formerly chemist for one of the large packing houses of Kansas City, then read a paper upon the subject "Cottonseed Oil and Its Uses in Commerce."

The author explained that the cottonseed oil is refined by a quick treatment with caustic soda. The refined oil is used in making a compound lard, a product composed of very little lard and a great deal of cottonseed oil, mixed with other animal fats. The liquid vegetable oil is solidified by means of chilled cylinders and mixed with the animal fats and lard. Another use is in the making of oleomargarine. Its composition is oleo oil, lard and cottonseed oil, the latter predominating in some commercial brands. It is also used in the preservation of sausages and in making so-called salad oil.

The most satisfactory test for cottonseed oil in olive oil and lard is the following, proposed by a French chemist :

Take 5 grams sample, add 0.8 gram powdered sulphur, 5 cc. carbon disulphide, and 5 to 8 cc. amyl alcohol. Immerse in boiling brine, and if cottonseed oil is present, a rosy coloration will take place in ten to fifteen minutes.

After discussing the paper and other points suggested by it, and giving the author a vote of thanks, the meeting was adjourned.

The ninth regular meeting was held on December 10, 1901, Professor Bailey presiding.

Dr. J. Robt. Moechel, the city chemist, read a paper entitled "Food Preservatives : Their Use, Abuse, and Toxicology."

The author makes a sharp distinction between the *use* and the *abuse* of preservatives. He makes the point that salt, saltpeter, creosote (in smoking meats), all time-honored preservatives, are "chemical preservatives" just as truly as are formaldehyde, salicylic acid, boric acid, etc., and that some of these newer preservatives may not be any more objectionable, if properly used. He thinks that the use of preservatives should be regulated by law, rather than prohibited.

He then takes up the various preservatives in detail, and the following are his conclusions in regard to them, many of which he reached through his own researches :

Borax, boric acid and boroglycerides slightly retard, but do not prevent digestion, are more effective than saltpeter, and cause probably less disturbances. They should be used in moderation.

Formic aldehyde, in very small quantities, is efficient. One part in 150,000 will make milk keep for two days. One part in 10,000 will preserve fruit for a reasonable length of time. One part in 1,000,000 is effective in wines. If used in these very small proportions, it is not detrimental in any way.

Sulphur dioxide and sulphites are objectionable, especially sulphites, which are distinctly toxic and injurious. Sulphur dioxide seems to be necessary in wines, but its use should be regulated by law.

Fluorides are distinctly injurious, and their use must be condemned.

Salicylic acid should be strictly limited in quantity, as it causes serious toxic effects unless taken in very small doses.

Benzoic acid and benzoates act similarly to salicylic acid and salicylates toxicologically. Indiscriminate use should be prohibited.

After the discussion, a motion was passed to thank the author, and have the paper preserved with the society records.

The secretary and treasurer's annual report was read and accepted.

A motion was passed to have this report printed and sent to the members, etc.

The councilor's report was made and accepted.

The annual election was then held, resulting in a reelection of all of the officers for the past year. The meeting was adjourned.

---

The tenth regular meeting was held on January 14th, with Professor Bailey in the chair.

The minutes were read and accepted.

Mr. E. C. Champion, assistant chemist of the Iola, Kansas, Portland Cement Works, presented a paper entitled "The Manufacture and Chemistry of Portland Cement."

After an interesting general talk on the chemistry and manufacture of Portland cement, the author described the rotary kilns (heated by natural gas) and other apparatus in use at the mills in Iola, Kansas, illustrating the various stages of its manufacture by specimens.

He finds the average ratio of lime to silica in nine leading brands, after deducting 1.1 times the amount of alumina present from the total lime, to be 2.51 instead of the theoretical 2.8, calculated in a like manner from the formula  $X(3\text{CaO}.\text{SiO}_2) + Y(2\text{CaO}.\text{Al}_2\text{O}_3)$ .

After the discussion, a motion was passed to thank Mr. Champion, and preserve his paper with the records of the society.

Mr. Burton Reid was appointed reporter.

The meeting was adjourned.

ARMAND R. MILLER, *Secretary*.

## Proceedings.

### NAMES PROPOSED FOR MEMBERSHIP.

Birdsong, J. H., Robertstown Furnaces, Bessemer, Ala.  
Dodd, Robert W., 1309 Guerrero St., San Francisco, Cal.  
French, Edmund L., Crucible Steel Co. of America, Syracuse,  
N. Y.  
Hanzlik, Vaclav, Box 553, Bay City, Michigan.  
Just, John A., 116 E. Castle St., Syracuse, N. Y.  
Miller, Harry H., Robertstown Furnaces, Bessemer, Neb.  
Mowry, Jesse B., Grand Island, Nebr.  
Overton, A. G., Robertstown Furnaces, Bessemer, Ala.  
Sanders, Warren W., 6428 Greenwood Ave., Chicago, Ill.  
Sloan, William H., Palo Alto, Cal.

### NAMES PROPOSED FOR ASSOCIATE MEMBERSHIP.

Arnold, R. B., 714 Ohio St., Terre Haute, Ind.  
Breed, Charles H., 7 Anoka Pl., Lynn, Mass.

### NEW MEMBERS ELECTED MARCH 10, 1902.

Behm, Albert, 2259 Woodstock St., Philadelphia, Pa.  
Hovey, Will. C., 106 Wabash Ave., Chicago, Ill.  
Langenbeck, Karl, Zanesville, O.  
Marx, J. S., Cal. Powder Works, Pinole, Cal.  
McKenna, A. G., Firth Sterling Steel Co., Demmler, Pa.  
Metzger, Floyd J., 361 W. 123rd St., N. Y. City.  
Oliver, Frank M., 755 N. 38th St., Philadelphia, Pa.  
Porter, J. Edward, Box 785, Syracuse, N. Y.  
Prindle, Harry B., 90 W. Broadway, N. Y. City.  
Rapalje, Ernest H., 12 John St., N. Y. City.  
Safford, E. B., 5 Oakland Crescent, Chicago, Ill.  
Zoul, Charles V., 6359 Normal Ave., Chicago, Ill.

### ASSOCIATES ELECTED MARCH 10, 1902.

Plank, W. F., State College, Pa.  
Wiedemann, H. Edmund, 944 N. 8th St., Terre Haute, Ill.

### CHANGES OF ADDRESS.

Bassett, Wm. H., Torrington, Conn.  
Busby, Fred. E., 14 Hoosac St., Adams, Mass.  
Campbell, G. F., Peoria, Ariz.

- Clark, Harry A., 349 Noble Ave., Bridgeport, Conn.  
Colley, B. T., Amer. Sm. and Ref. Co., Omaha, Nebr.  
Cushman, Allerton, S., Dept. of Agr., Washington, D. C.  
Fischer, Robert, 619 Delaware Ave., Wilmington, Del.  
Goodman, Julian H., 149 W. 35th St., New York City.  
Howard, A. P., 75 Broad St., Boston, Mass.  
Hunter, H. B., 6 E. 32nd St., New York City.  
Morgan, W. C., 2121 Durant Ave., Berkeley, Cal.  
Mork, H. S., 7 Exchange Pl., Boston, Mass.  
Nagelvoort, J. B., 507 Madison St., Topeka, Kansas.  
Neilson, Thomas, Triunfo, B. Calif, Mexico, via Nogales and Guaymas.  
Robeson, F. W., Agricultural College, Mich.  
Rücker, H. von, 493 Twelfth St., Brooklyn, N. Y.  
Shaw, H. I., Kendall, Mont.  
Sherman, Geo. W., care Western Rubber Co., Ltd., Litherland (near Liverpool), England.  
Stillwell, J. S., 156 Broadway, New York City.  
Summey, A. E., Painted Post, N. Y.  
Terry, H. Warren, Jr., 2029 Mt. Vernon St., Philadelphia, Pa.  
Torrey, Joseph, Jr., 515 West Market St., Akron, O.  
Wallace, E. C., 646 West End Ave., New York City.  
Weissmann, F. W., S. W. cor. Vine and University Aves., Cincinnati, O.



## Proceedings.

### NAMES PROPOSED FOR MEMBERSHIP.

- Evanson, A. A., Aetna, Ind.  
Gibson, Charles B., Room 39, 81 S. Clark St., Chicago, Ill.  
Goslan, Justus E. W., 177 Broad St., Newark, N. J.  
Ingham, Leslie H., Kenyon College, Gambier, O.  
Kalbfleisch, Franklin H., 31 Burling Slip, New York City.  
Knight, Ora W., 84 Forest Ave., Bangor, Me.  
Langley, Clifford, 64 Irving Place, New York City.  
Lomox, Clarence S., New England Gas and Coke Co., Everett,  
Mass.  
• McClure, Clyde H., 724 Forest Ave., Oak Park, Ill.  
Moorhouse, Wm. R., Lowell Textile School, Lowell, Mass.  
Queneau, Augustin L. J., 439 Manhattan Ave., New York City.  
Reed, Charles J., 3313 N. 16th St., Philadelphia, Pa.  
Richmond, Francis A., Elmira College, Elmira, N. Y.  
Starke, Eric A., Pacific Coast Oil Co., Alameda, Cal.  
Simonds, Ernest H., 417 Montgomery St., San Francisco, Cal.  
Stofer, Richard C., 28 Hayes St., Norwich, N. Y.  
Walters, Harry E., 4 Shetland Ave., East Liberty, Pittsburg, Pa.  
Williams, Stanley M., 269 Springdale Ave., E. Orange, N. J.

### NEW MEMBERS ELECTED MARCH 29, 1902.

- Aldrich, Charles H., Perth Amboy, N. J.  
Adler, Leon L., 100 William St., N. Y. City.  
Arey, Albert L., 1148 Pacific St., Brooklyn, N. Y.  
Ash, Charles S., 141 Fell St., San Francisco, Cal.  
Barber, René R., Georgetown, Ontario, Canada.  
Bauer, G. W., 1722 Buchanan St., San Francisco, Cal.  
Bird, R. M., Agricultural College, Miss.  
Carter, John P., 626 S. 24th St., Philadelphia, Pa.  
Cohn, Alfred L., 14 E. 97th St., N. Y. City.  
Eckart, Charles F., Honolulu, H. I.  
Ellis, Wm. H., School of Practical Science, Toronto, Canada.  
Harrell, George R., Copperfield, Vt.  
Haynes, Herman W., 3 Dudley Place, Worcester, Mass.

- Kennedy, Mortimer B., 523 Madison St., Ann Arbor, Mich.  
 Kinney, Charles N., Drake University, Des Moines, Iowa.  
 Klein, Arthur, Box 678, Erie, Pa.  
 Krayner, Stephen S., care of Chas. Pfizer & Co., 11 Bartlett St., Brooklyn, N. Y.  
 Lang, Wm. R., University of Toronto, Toronto, Canada.  
 Lawson, William, Alameda Sugar Co., Alvarado, Cal.  
 Lee, Theophilus H., care of Mr. F. D. Aller, Antofagasta, Chili, South America.  
 Mathews, Albert P., University of Chicago, Chicago, Ill.  
 McNulty, William P., 21 Gold St., Norwich, N. Y.  
 McQueen, H. J., El Dorado Oil Works, West Berkeley, Cal.  
 Morse, Willard S., Apartado A, Aguascalientes, Mexico.  
 Oliver, Roland, L., 101 Vernon St., Oakland, Cal.  
 Perley, William M., 1846 East Belmont Ave., Chicago, Ill.  
 Robinson, Franklin C., Bowdoin College, Brunswick, Me.  
 Sampson, (Miss) Ethel V., 957 Washington St., Newtonville, Mass.  
 Searby, F. W., El Dorado Oil Works, West Berkeley, Cal.  
 Shoemaker, Harry I., 4205 Mason Ave., Tacoma, Wash.  
 Smith, Francis P., 124 Sansome St., San Francisco, Cal.  
 Snow, Frank J., Chem. Lab., Internal Revenue Office, Appraisers' Building, San Francisco, Cal.  
 Taylor, M. A., 25 East St., New Castle, Pa.  
 Tompkins, Philip W., 123 California St., San Francisco, Cal.  
 Werner, David T., 114 South 9th St., Lebanon, Pa.

#### ASSOCIATES ELECTED MARCH 29, 1902.

- Collins, Ward C., 3424 Wabash Ave., Chicago, Ill.  
 Simmons, John P., 46 Park Ave., Yonkers, N. Y.

#### CHANGES OF ADDRESS.

- Arnold, Frank L., care Bowker's Fertilizer Co., St. Bernard, Ohio.  
 Cady, W. B., 602 Packard St., Ann Arbor, Mich.  
 Cuadrado, Gaston A., Lab. Quim, Merced 77, Havana, Cuba.  
 Eldred, Frank R., Ligonier, Ind.  
 Finke, Alfred H., 409 East 5th St., Cincinnati, O.  
 Hoff, Karl, 408 Birch St., Anaconda, Mont.  
 Kendall, E. Dwight, 33 Lincoln Road, Brooklyn, N. Y.  
 Meade, Richard K., care Edison Portland Cement Co., Stewartsville, N. J.  
 Nagelvoort, J. B., 16 Mulberry St., Detroit, Mich.  
 Neumeister, E. J., Bay City, Mich.  
 Nikaido, Y., Leavitt, Nebr.  
 Pearce, E. D., Box 1336, Providence, R. I.  
 Phalen, W. C., 15 Raven St., Dorchester, Mass.  
 Thompson, G. W., 129 York St., Brooklyn, N. Y.

Thurlow, Nathaniel, care Ampère Electro-Chemical Co.,  
Niagara Falls, N. Y.

Waters, C. D., care of Morrison & Cass Paper Co., Tyrone, Pa.  
Wrampelmeier, T. J., 318 Front St., San Francisco. Cal.

**ADDRESSES WANTED.**

Brown, C. Arthur, formerly of 630 W. 8th St., Cincinnati, Ohio.  
John P. Terry, formerly of Anaconda, Mont.

---

**DECEASED MEMBERS.**

Mr. Hugh Lee Miller, member of the Society since 1895, District Manager (for South Carolina) of the Virginia-Carolina Chemical Co., died in Columbia, S. C., February 5, 1902.

Samuel S. Taite, of Philadelphia, who had but just joined the Society, died February 23, 1902. He was a recent graduate of the University of Pennsylvania, and a young man of great promise.

Albert R. Leeds, Professor of Chemistry in Stevens Institute, Hoboken, N. J., since 1871, and member of the Society since 1878, died March 13, 1902. He was for years one of the most energetic and devoted workers of the Society, and was Vice-president from 1877 to 1888, and again in 1892.

Joseph Richards, of Philadelphia, member of the Society since 1900, died March 22, 1902. He was a man of attractive personality, and of broad experience as a metallurgical chemist, and had been President of the Metallurgical Section of the Franklin Institute.

---

**MEETINGS OF THE SECTIONS.**

**MICHIGAN SECTION.**

The Michigan Section met on Friday, March 28th, at the University of Michigan, Professor Campbell presiding. The following papers were presented :

"Michigan as a Beet Sugar State." By P. F. Trowbridge.

"Solubility of Calcium Carbonate in Water Free from Carbon Dioxide." By H. E. Brown.

"Solubility." By G. A. Hulett.

"The Volumetric Estimation of Alumina and Free and Combined Sulphuric Acid in Alums. By A. H. White.

The election of officers resulted as follows :

*President* : E. D. Campbell, Ann Arbor.

*Member of Council* : M. Gomberg, Ann Arbor.

*Secretary-Treasurer* : A. H. White, Ann Arbor.

*Elective Members of Executive Committee* : S. G. Jenks, Kalamazoo ; P. F. Trowbridge, Crosswell ; O. Button, Wyandotte.

ALFRED H. WHITE, *Secretary*.

#### WASHINGTON SECTION.

The 133rd regular meeting of the Chemical Society of Washington was held March 12th. The following program was presented :

"Common Errors in the Determination of Silica." By W. F. Hillebrand. This paper was also presented by Dr. Hillebrand at the winter meeting of the American Chemical Society, and was published in the April number of this Journal.

"Researches on the Oxides of Tungsten." By E. T. Allen.

1. When tungstic acid is reduced by stannous chloride at 100° C., or by hydriodic acid in sealed tubes at 200° C., the product is an indigo-blue powder of the composition  $W_3O_{11} \cdot H_2O$ . This compound is changed to tungstic acid by most oxidizing agents. In hydrochloric acid it is insoluble. Caustic alkalis dissolve it with evolution of hydrogen and formation of alkaline tungstate. So far, no salt has been obtained from it. Its formula agrees with that of the blue oxide of molybdenum,  $Mo_3O_{11} \cdot 6H_2O$ , recently studied by Guichard.

2. Concentrated ammonia extracts tungstic acid from the blue oxide, leaving a residue which is purple with a strong bronze luster. Its formula is  $W_3O_{11} \cdot H_2O$ . The chemical properties of this body are similar to those of the blue oxide. Thus it is insoluble in hydrochloric acid, soluble in caustic alkalis with evolution of hydrogen and more readily attacked by oxidizing agents than the blue oxide. It finds an analogue among the oxides of uranium ( $U_3O_{11} \cdot xH_2O$ ).

3. In composition and color these two oxides are closely related to the tungsten bronzes. Thus we have  $W_3O_{11} \cdot M_2O$ , where  $M_2 = K_2, Na_2, Li_2$ , or  $Ba$ , all *dark blue* in color ; and  $W_3O_{11} \cdot M_2O$ , where  $M_2 = Na_2$ , or  $K_2$ , both having a metallic luster, while  $W_3O_{11} \cdot K_2O$ , described by Hallopeau as a reddish violet powder with a copper reflex, recalls  $W_3O_{11} \cdot H_2O$  in a striking way. Direct transformations of these bronzes into the two oxides mentioned in this paper, or *vice versa*, have not been accomplished.

L. S. MASON, *Secretary*.

## Proceedings.

### NAMES PROPOSED FOR MEMBERSHIP.

Aydelott, Charles G. B., Maple and Ridgewood Aves., Norwood, O.

Brady, Wm., 7642 Marquette Ave., Chicago, Ill.

Burr, H. M., 165 Prospect Park West, Brooklyn, N. Y.

Campbell, A. H., 813 20th St., Oakland, Cal.

Clay, G. Harry, Winton Place, O.

Devlin, John A., Lawrence, Kans.

Doveton, Godfrey D., Cyanide Works Camp Bird Mills, Ouray, Colo.

Dunham, Andrew A., 74 John St., N. Y. City.

Haas, Herbert, Torreon, Coahuila, Mexico.

Hermes, Edward, 979 Parsons Ave., Columbus, O.

Hewett, Foster, 66 Church St., Bethlehem, Pa.

Kawin, C. C., 1424 Fulton St., Chicago, Ill.

Lindauer, Arthur M., 3312 Calumet Ave., Chicago, Ill.

Lippincott, Jesse T., 261 E. Auburn Ave., Cincinnati, O.

Ludlow, S. H., Cement City, Mich.

Meyer, August R., 404 New England Bldg., Kansas City, Mo.

Miller, Robert N., Male High School, Louisville, Ky.

Mott, Wm. A., Mayfield, Ky.

Neal, Frank, Care Acme White Lead and Color Works, Detroit, Mich.

Petsche, B. W., 25 Fairview St., Yonkers, N. Y.

Putnam, Wm. P., care of American Radiator Co., Chicago, Ill.

Rich, Charles H., Duquesne, Pa.

Richardson, Leon B., Hanover, N. H.

Roe, J. Newton, Valparaiso, Ind.

Rogers, Roy R., 2528 Union St., San Francisco, Cal.

Rounds, M. B. C., Aurora, Ill.

Schwarz, H. P., Western Sugar Ref. Co., Potrero, San Francisco, Cal.

Smith, Robert C., 425 Home Ave., Oak Park, Ill.

Stoddard, Jesse D., care of Operating Board, American Radiator Co., Chicago, Ill.

Vannier, Charles H., 1623 Fulton St., Chicago, Ill.  
Waldenberger, Chas. A., 155 E. 37th St., N. Y. City.  
Wilson, R. N., Guilford College, N. C.  
Witherell, Frederick W., Winchester, Mass.

NAMES PROPOSED FOR ASSOCIATE MEMBERSHIP.

Haines, J. Hilyard, 2130 S. 15th St., Philadelphia, Pa.  
Thomas, Elmer L., 31 Nassau St., N. Y. City.

NEW MEMBERS ELECTED APRIL 17, 1902.

Birdsong, J. H., Robertstown Furnaces, Bessemer, Ala.  
Dodd, Robert W., 1309 Guerrero St., San Francisco, Cal.  
French, Edmund L., Crucible Steel Co. of America, Syracuse,  
N. Y.  
Hanzlik, Vaclav, Box 553, Bay City, Mich.  
Just, John A., 116 E. Castle St., Syracuse, N. Y.  
Miller, Harry H., Robertstown Furnaces, Bessemer, Ala.  
Mowry, Jesse B., Grand Island, Nebr.  
Overton, A. G., Robertstown Furnaces, Bessemer, Ala.  
Sanders, Warren W., 6428 Greenwood Ave., Chicago.  
Sloan, William H., Palo Alto, Cal.

ASSOCIATES ELECTED APRIL 17, 1902.

Arnold, R. B., 714 Ohio St., Terre Haute, Ind.  
Breed Charles H., 7 Anoka Place, Lynn, Mass.

CHANGES OF ADDRESS.

Arnold, F. L., P. O. Box 233, St. Bernard, Ohio.  
Baxter, Wm. T., N. Y. C. and H. R. R. Lab., West Albany,  
N. Y.  
Bird, Maurice, Moody Hotel, Hot Springs, Ark.  
Bolling, Randolph, Supt. Blast Furnace, Care Va. I. C. & C.  
Co., Buena Vista, Va.  
Broadhurst, W. H., 294 Lafayette Ave., Brooklyn, N. Y.  
Cady, W. B., Cement City, Mich.  
Cayvan, L. L., 817 Penna. Ave., Kansas City, Mo.  
Chamberlain, J. S., U. S. Dept. of Agr., Washington, D. C.  
Davis, W. Walley, Care Va. I. C. & C. Co., Roanoke, Va.  
Dean, J. G., 810 Union Trust Bldg., Detroit, Mich.  
Dorr, John V. N., Care Lundberg and Dorr, Deadwood, S. D.  
Felt, W. W., 6912 Parnell Ave., Englewood, Chicago, Ill.  
Fetterolf, D. W., Chem. Lab., Med. Dept., Univ. of Pa., Phila-  
delphia, Pa.  
Fischer, Robert, 804 Adams St., Wilmington, Del.  
Gallaher, P. C., Care Iron Silver Mining Co., Leadville, Colo.  
Goodell, Geo. A., Mirror Lake, N. H.  
Goodmar, Julian H., Dyeing Dept., Yorkshire Coll., Leeds,  
Eng.

Herreshoff, J. B. F., 40 W. 69th St., N. Y. City.  
 Hosch, George E., 55 Bogart St., Brooklyn, N. Y.  
 Lazell, E. W., 1416 So. Penn Square, Philadelphia, Pa.  
 Linebarger, C. E., 740 Cullom Ave., Ravenswood, Chicago,

## III.

Lippincott, W. B., 3620 Genesee St., Kansas City, Mo.  
 Loeser, R. M., Box 142, Stanford University, Cal.  
 Meaker, W. L., Daiquiri, Santiago de Cuba, Cuba.  
 Mersereau, Gail, 365 Manhattan Ave., N. Y. City.  
 Moffatt, Miles R., care of Mallinckrodt Chem. Works, St. Louis,

## Mo.

Montgomery, Jack P., 5613 2nd Ave., S., Woodlawn Sta., Birmingham, Ala.

Moyer, J. Bird, 1947 N. 18th St., Philadelphia, Pa.  
 McDowell, Alex. H., 373 W. 123rd St., N. Y. City.  
 McKenna, A. G., 506 Hawkins Ave., Braddock, Pa.  
 Nagelvoort, J. B., 16 Mulberry St., Detroit, Mich.  
 Nikaido, Y., Leavitt, Nebr.  
 Norris, R. S., Alhambra, Cal.  
 Oglesby, W. R., Stroth, La Grange Co., Ind.  
 Pierson, W. C., Box 630, Atlanta, Ga.  
 Pritchard, F. P., 6441 Jackson Ave., Chicago, Ill.  
 Ransom, A. McB., 205 Spring St., Atlanta, Ga.  
 Sarles, E. H., Stelton, N. J.  
 Schwartz, David, Southern Cotton Oil Co., Gretna, La.  
 Seldner, Rudolph, 1395 Dean St., Brooklyn, N. Y.  
 Sinkinson, J. D., 97 Norman Ave., Greenpoint, Brooklyn, N. Y.  
 Smith, Theodore E., 44 Hudson Place, Sta. 1, Hoboken, N. J.  
 Smoot, A. M., 1263 Waverly Pl., Elizabeth, N. J.  
 Stalnaker, E. S., Morgantown, W. Va.  
 Stone, Geo. C., Care N. J. Zinc Co., 11 Broadway, N. Y. City.  
 Strahorn, A. T., 205 William St., N., Goldsboro, N. C.  
 Sutro, H. H., 126 Liberty St., N. Y. City.  
 Swett, Chas. E., 179 Medway St., North Sta., Providence, R. I.  
 Vulté, H. T., 437 W. 59th St., N. Y. City.  
 Wallace, E. C., 646 West End Ave., N. Y. City.  
 Wigfall, E. N., Addingham, Pa.  
 Wilkens, H. A. J., 11 Broadway, N. Y. City.  
 Zoul, Chas. V., 1543 W. 22nd St., Chicago, Ill.

## ADDRESS WANTED.

George F. Campbell, formerly of Peoria, Ill.

---

 DECEASED MEMBERS.

Professor Albert Ripley Leeds was born in Philadelphia, June 27, 1843. He descended from a long line of Americans, many of

whom achieved distinction in engineering and scientific pursuits. The colonist of his name was in 1680 the surveyor-general of New Jersey, and was the publisher, through William Bradford, printer, of the first book in America published south of the Massachusetts Bay colony.

Professor Leeds graduated from the high school of Philadelphia in 1860, and entered Harvard University, remaining there during the four years of the civil war, and taking his degree in 1865. Before graduation he was appointed professor of chemistry in the Philadelphia High School, and during the following year he held also similar chairs in the Franklin Institute, the Philadelphia Dental College, and Haverford College. The three latter professorships necessitated incessant lecturing and teaching, and in the attempt to discharge these duties his health broke down. Resigning them in 1869 he went abroad and spent two years in travel and study in England, France, Germany and Italy.

On his return he was requested to organize the department of chemistry at the Stevens Institute of Technology, then a comparatively new institution of learning. He became professor of chemistry, and for thirty years devoted his highest talents to teaching. So faithful and conscientious was his work that he came to occupy an important place in the faculty, and was honored and loved by his students, to whom he taught not only chemistry, but manhood. His personality influenced all those with whom he came in contact, and in his last days it was a source of gratification to him that "all of his boys had turned out well."

Dr. Leeds early acquired a reputation as an expert chemist. His first attention was given to mineralogy and lithology, but he soon became interested in water analysis and sanitary science, the field in which he was most widely known. Still later he became an expert in the analysis of milk and various food products. For many years he was chemist to the water boards of Newark and Jersey City, and to the Hackensack Water Company, and made important investigations of the water supplies of Albany, New London, Jamestown, Philadelphia, Reading, Plymouth, Wilmington, Ottawa, and other cities. One of his most important water investigations was made for the City of Brooklyn in 1896. This was made the subject of a voluminous report which attracted wide-spread attention. Dr. Leeds was one of the earliest chemists



to appreciate the value of the use of alum as an aid to the filtration of water, and was often called in by filter companies to give expert testimony. Although his ideas for many years met with opposition, he lived long enough to see mechanical filtration with the use of alum take its place as a well recognized process, and one which has the endorsement of the engineering profession.

Professor Leeds occupied many important public positions. In 1878 the College of New Jersey conferred upon him the degree of doctor of philosophy. It was well merited, for he it was who gave a start to the development of sanitary science in that state. For many years from 1881 he was a member of the New Jersey State Board of Health and chairman of its Council of Analysts. In 1886 he was elected a foreign member of the British Association for the Advancement of Science. He was also a member of the American Society of the same name, the American, English, and German Chemical Societies, the American and New England Water Works Associations, the Franklin Institute, and various art societies and social organizations. Dr. Leeds was present at the meeting at which the American Chemical Society was organized in 1876, and during the first decade of the history of the Society he was one of its most active members. For many years he was one of the vice-presidents and member of the board of directors, besides being chairman of the Publication Committee. To no member does the society owe a greater debt for earnest and faithful labor than to Professor Leeds. His interest in the Society was always maintained, though in recent years increasing deafness caused him to give up frequent attendance at the meetings.

Dr. Leeds published more than one hundred scientific memoirs and reports. They include nine papers on new minerals and the lithology of the Adirondacks; thirty-eight papers on analytical chemistry published in the *Zeitschrift*, the *Chemical News*, the *American Journal of Science*, and elsewhere; forty-two papers on technical and general chemistry published in the journals of the *American Chemical Society* and the *New York Academy of Science*; besides numerous papers on water analysis, sanitary science, foods and food adulteration, etc., published in various scientific journals.

Great as was his interest in science, his love of art, literature and music was greater; and it is because of these non-scientific pursuits that the life of Professor Leeds is especially worthy of the

consideration of his fellow scientists. Too often a scientist is only a scientist, and lacks in power through want of the stimulating influences of the great leaders of thought in fields different from his own.

In Professor Leeds the art instinct was inborn, and he did not neglect its cultivation. While at Harvard he had the good fortune to become intimately acquainted with James Russel Lowell, at whose house he was a frequent visitor and with whom he read Dante and Faust in the original. He was often present at Lowell's Sunday night teas, and there he had the pleasure of meeting such men as Longfellow, Dr. Holmes, Professor Asa Gray and Louis Agassiz. Dr. Leeds always looked back on these days as the "Golden Age of Harvard." He cherished a deep affection for his Alma Mater, and on revisiting Cambridge a few years before his death he was greatly pleased to learn that his old room at college had, since his day, been occupied by President Roosevelt. He never gave up his literary studies, so happily begun. Throughout his life it was his custom to read a few verses daily from the Greek Testament. He read fluently in the Latin, Greek, French, German, Italian, and Spanish languages, and his journals, kept for his children, abound in quotations from the ancient poets, and from the great works of literature. Painting and architecture, however, attracted him most, and some of his most intimate friends were sculptors and artists.

He had also the creative instinct, and his charcoal sketches made on the Rhine, his translations of the Odes of Horace, his essays on Dante and Ruskin, delivered sometimes to a small coterie of friends on Sunday afternoons, and again to clubs of working-men; his architectural designs of cottage and fireplace, drawing-room and rose-bower attest the versatility of his genius. His "Meditations," written at Cotton Hill, his New Hampshire summer home, are charming in their simplicity and depth of feeling.

The home life of Dr. Leeds approached the ideal, as all who were ever entertained by him will bear witness. In 1871 he married Miss West, the great granddaughter of General Reed, first president of the State of Pennsylvania. In 1891 he married Miss Webb, daughter of William H. Webb, the secretary of the Reading Railroad. His wife and two daughters survive him.

It was in his last days, when he knew that death would soon overtake him, that the loveliness of his character shone forth. Stevenson himself was not more brave or cheerful, and those who met him to say farewell received a lesson in Christian fortitude that they will never forget. Only a few days before his death, which occurred at Philadelphia, on March 13, 1902, some of the undergraduates of Stevens Institute went to his home and presented him with a loving cup; and it is doubtful if, in all his life, he did anything of more lasting value than this farewell address to his students. His zeal, his courtliness, his kindness, and his simplicity, his love of truth and beauty, and, above all, his serene heroism in the presence of death, were made manifest as on no other occasion.

Professor Leeds always had a deep sense of the dignity and responsibility of his calling, yet he held his own service in modest appreciation. His words to the writer as he said "good-bye" on his last visit to his laboratory were an illustration of this. On being asked if he would be at the laboratory on the following week, he looked around him with a smile and said, "For thirty years I have worked in this little shop; I have done little, but I have tried to serve well my day and generation. When I leave it to-day I shall never come back. Others can do the work now. As for me, I'll go to "Roadside" and lie down."

GEORGE C. WHIFFLE.

Mr. R. F. Means, of Boston, Mass., member of the Society since 1899, died suddenly of heart failure, April 8, 1902.

Mr. Charles Q. Rawling, of Wheeling, W. Va., member of the Society since 1894, died March 5, 1902.

Dr. Henry Morton, president of Stevens Institute, Hoboken, N. J., since its foundation in 1870, died May 9, 1902. Dr. Morton was one of the original members of the American Chemical Society, and was one of its vice-presidents during the first two years, and again in 1881.

Mr. William Sanford Robinson, of Omaha, Nebr., engineer of tests for the Union Pacific Railroad, member of the Society since 1894, died March 29, 1902.

---

## MEETINGS OF THE SECTIONS.

### CHICAGO SECTION.

February 4th, a public lecture was given by Professor C. F. Chandler on "The Electrochemical Industries at Niagara Falls." The lecture was held in the chemical auditorium of the Northwestern University, and was attended by a very large audience. The lecture was illustrated with a complete set of specimens. Previous to the lecture, Professor Chandler was entertained at an informal supper, giving the section an opportunity of meeting and greeting him. Professor Chandler came especially to Chicago to deliver this lecture and the section takes this opportunity of thanking him for his great courtesy in favoring it with a most interesting and highly instructive discourse.

March 26th, a paper was read by Professor S. W. Parr, of the University of Illinois, on "Coals of Illinois and their Calorific Determination." The paper was illustrated, and various forms of apparatus used in making the determinations were shown and explained.

April 24th, a paper was read by Professor Cass L. Kennicott on "Practical Water Softening." The paper was illustrated with charts and practical experiments and was freely discussed, especially by chemists of various railroad companies, some of whom came quite a distance to attend the meeting.

Papers announced: "Manufacture and Analyses of Alloys," by Dr. A. Thurnauer, Aurora Metal Co.; "Borax," by Dr. S. T. Mather, manager Pacific Coast Borax Co.

The Chicago Technical Club have placed their rooms at the disposal of the section and all future meetings will be held there.

W. A. CONVERSE, *Secretary*

### NEW YORK SECTION.

At the regular May meeting (held May 9, 1902) of the New York Section there were 128 members present. Two very important matters of business came before the attention of the Section. The chairman, Professor Marston Taylor Bogert, announced that as the result of the vigorous movement set on foot early in the year, a research medal had been endowed, to be awarded annually by the New York Section. Mr. William H.

Nichols, a charter member of the American Chemical Society and president of the General Chemical Company, has conveyed to the Society, in trust for the New York Section, securities to the value of over \$1,000 to endow the annual award of a gold medal to be presented by the New York Section to the author who presents the best paper to the section embodying original chemical research. It is not intended to limit the competition to members of the section or even of the Society. The only other conditions thus far imposed are that the paper be subsequently published in the Journal of the Society, and that it be of sufficient merit to deserve the award of the "William H. Nichols Medal of the New York Section."

Dr. Maximilian Toch, chairman of the Committee on Research Fund and Medal, announced that other members of the Section had contributed nearly enough to provide for the securing of a beautiful original design and die for the medal which Mr. Nichols' generosity guarantees in perpetuity.

Resolutions expressing the thanks of the Section to Mr. Nichols were presented by Professor Bogert, seconded by past-president of the Society, Dr. McMurtrie, and enthusiastically adopted by the members present.

The second important item of business needs no further comment than the perusal of the following resolution which was adopted by a *unanimous* vote.

"*Resolved*, That, in the judgment of the New York Section of the American Chemical Society, the existence of an 'associate membership' constitutes a serious obstacle to the proper growth and development, not only of the Society as a whole, but especially of this local section; that a discrimination of this kind, which does not exist in other chemical societies of the world, is entirely unwarranted and unnecessary, aside from the difficulty of enforcing it justly; that it prevents the securing of many most desirable members who will not join as 'associates,' and accomplishes no good purpose, raising, as it does, an insurmountable barrier to the union in one great national chemical society of all interested in the science or practice of chemistry, an attitude which has already resulted in the founding of separate societies of Chemical Industry (New York Section), Physiological Chemistry, and Electrochemistry, in which no such invidious distinctions are made and where all meet upon the same level.

" Further, that the members of the New York Section hereby request their representatives in the Council to endeavor to secure such legislation by the parent society as shall abolish 'associate membership' and place all members upon the same footing.

" Also, that copies of these resolutions be printed and forwarded to all members of the Council of the American Chemical Society and of the New York Section."

JOHN ALEXANDER MATHEWS, *Secretary*











